STATE-OF-THE-ART REVIEW OF CERAMIC-
TO-METAL JOINING

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FOREWORD

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ABSTRACT

A state-of-the-art review of the joining of crystalline ceramic parts
to metal parts is presented. This study was undertaken to evaluate the
current status of ceramic-metal joining, particularly in relation to its
advancement in t. e past decade, and to develop unifving principles which
could lead to more effective joining techniques. The mechanical and
chemical methods used in the fabrication of structural and electronic
components, with and without hermetic requirements, were considered in-
cluding the general requirements and limitations of the components without
regard to specific areas of utility.

All major facets of the technology were covered under joining techniques,
materials, apparatus, theories and test methods. Background information
was obtained from an extensive survey of domestic and foreign literature
and from field research based on a questionnaire survey and personal inter-
views. On the basis of the information collected, each major aspect of the
technology is critically reviewed and recommendations for future improvements
are advanced in this report.

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1. Introduction

1.1 Purpose and Scope

The purpose of this report is to review the state-of-the-art of ceramic-to-metal joining technology as it exists today, particularly in relation to the advances made during the past decade. All major facets of permanently joining metal parts to crystalline ceramic parts have been assessed in the light of the deficiencies, the present needs, and the future technological requirements. Methods of joining, whether by solid or liquid phase bonding or by prior metallizing, are described and discussed. Applications of the various fabricating methods have been delineated in relation to the areas of utility rather than in terms of specific products. The present status and needs in materials are surveyed for the major metal and ceramic components and for the accessory materials which are used to effect a joint. The equipment and apparatus used for ceramic-to-metal joining are examined in general terms in relation to the effectiveness and efficiency with which it is utilized. Test methods used to determine the integrity and reliability of ceramic-metal joints are described and critically surveyed for adequacy. The nature of the bond between ceramics and metals is reviewed as a basis for a critical examination of the existing specialized explanations of ceramic-to-metal bonding. Throughout the study, emphasis was placed on the formulation of unifying principles on which new advances could be mounted. Information was collected from such related fields as coatings, cermets, granular and fibrous dispersions and glass-to-metal sealing even though these fields, per se, are not discussed in this report.

Although ceramic-to-metal joining has seen application in electronic and electrical components, in aerospace and naval structures, in machine tooling, and in many other fields, the technology as applied to electronics, primarily, and to aerospace, to a lesser degree, was most frequently encountered in this survey and therefore has been stressed in this report. This is not to imply that the other areas of application are unimportant or of only passing interest. Rather, the technology of ceramic-to-metal joining was begun, developed and found its greatest usage in the electrical/electronic industry. The applications to other spheres of endeavor have been, by and large, adaptations of the basic joining principals which had been successfully used and proven by the electrical/electronics industry. In some cases, an extension of these principles to more severe environments or more exotic requirements has advanced the state-of-the-art beyond the more common requirements.

1.2 Approach

This report is the product of an extensive literature search of American and foreign technical articles, patents, and Government reports.

The literature retrieval was performed by library personnel at Texas Instruments Incorporated and was accomplished by searching abstract sections of scientific journals, engineering indexes, and listings of Government reports. Early in this program it became apparent that five sources supplied a nearly complete coverage of ceramic-to-metal joining references for the past decade. These are:

> Ceramic Abstracts (American Ceramic Society)
> British Ceramic Abstracts (British Ceramic Society)
> Chemical Abstracts (American Chemical Society)
> Metallurgical Abstracts (Institute of Metals-British)
> Nuclear Science Abstracts (U.S.Atomic Energy Commission)

Searching for earlier publication, therefore, was concentrated on these sources. Government reports were cross-checked by searching Scientific and Technical Aerospace Reports and the Technical Abstract Bulletins of Defense Documentation Center. A computer search of reports of Government-sponsored investigations in the field of ceramic-to-metal joining was conducted by Defense Documentation Center. The search covered both unclassified and classified (to the level of Secret) literature. Nothing of a classified nature, however, is contained in this report. Abstracts of more than six hundred technical articles, an equal number of patents, and about three hundred and fifty Government reports were examined for pertinency and approximately seventy-five per cent of the complete documents were studied.

Early in the program a questionnaire was sent to approximately three hundred individuals who were engaged in ceramic-to-metal joining production, application, development, or research, requesting information on joining and test methods. Forty-three per cent of the questionnaires were completed and returned, many with expansive appended notes on processes and test methods or comments on the state-of-the-art. Unpublished articles and preprints of recently written papers were generously volunteered with many returned questionnaires. Based on the questionnaire returns, a series of informal talks with many individuals prominent and knowledgeable in the field were held. Time and budget limits imposed restrictions on the personal interview phase of the program and no attempt was made to gather the opinions of more than a small percentage of the users, producers, and investigators in the field. Although many persons of prominence had no opportunity to present their views, it is felt that the persons interviewed represent a good cross-section of opinion on the state-of-the-art of ceramic-to-metal joining. Information from the questionnaires and interviews was used throughout the report but has not been tabulated or referenced outside of the bibliography.

1.3 Organization of the Report

Throughout the literature and field research, information was collected and categorized into five important aspects of ceramic-to-metal joining. These categories have been used for the basis of this report as follows:

a. Methods of fabrication, whether applied to production methods or laboratory techniques.

b. Design and materials considerations, as general classifications rather than specific products.

c. Equipment, described as the types of apparatus utilized and its function.

d. Testing methods, as general principles rather than specific procedures.

e. Theory of joining, considered on the basis of present specialized explanations of ceramic-to-metal joining and the more fundamental explanations of interatomic bonding.

The order in which these topics are discussed is not a reflection of their importance but rather a logical way of presenting the information. In each case, a list of references to published literature which is directly related to the discussion is provided, rather than a compilation of an extensive bibliography of all the material which was surveyed. References, especially to fabrication processes, are typical and give ample descriptions of the subject being discussed and are not necessarily cited as the classic documents in the particular field.

2. Methods of Fabrication

2.1 General and Historical

On June 20, 1939, four U.S. patents[1] were issued to Pulfrich and Magner of Germany, relating to ceramic-to-metal seals. These patents were assigned to the General Electric Company but if any notice was made of their existence, no serious action was taken on their development outside of Germany. Approximately six and a half years later, the office of Military Government for Germany (U.S.) released a report[2] which detailed the development and production work which had been carried out on practical ceramic-to-metal vacuum tubes by Pulfrich and his group in Germany in the closing years of World War II. This report provided the impetus for a series of investigative programs aimed at duplicating and improving the process of ceramic-to-metal joining. During this period, the work of Bondley,[3] Nolte and Spurck,[4] Pearsall and Zingeser,[5] Wellinger,[6] and others provided the groundwork for the ceramic-to-metal joining processes which are being used in a large segment of the industry today. In April 1953 a Symposium on Ceramics and Ceramic-Metal Seals, sponsored by the Research Development Board, was held at Rutgers University, New Brunswick, N. J. The collected papers of this meeting were published in Ceramic Age magazine in 1954[7] and represented the state-of-the-art as it existed at the mid-point of the last decade.

The period from the mid-fifties to the mid-sixties can perhaps be termed the "coming of age" of ceramic-to-metal joining. Processes were taken out of the research and development areas and applied as production methods. New methods, as typified by the reactive alloy seals developed by Beggs[8] and Wisser and Hagadorn,[9] evolved from the existing techniques. More thought was given to the mechanisms of ceramic-to-metal joining as bond theories were sought. An awareness of the necessity for control of materials, processes and finished products grew as requirements for more and better joined assemblies increased. Aerospace applications and increased reliability requirements spurred research into new methods of joining such that many reliable joining methods exist today.

2.2 Joining Systems

Methods of obtaining an intimate, permanent joint between a metal member and a ceramic member can be divided into three systems. As in any such attempt to classify subjects, the boundary lines are not absolute. These three systems will, for the sake of simplicity, be termed solid phase joining, liquid phase joining, and metallizing. (Refer to Table 1)

2.2.1 Solid Phase Joining

In this system, initial contact between the members is obtained mechanically but final, intimate, free-standing contact remains after the mechanically-induced forces are removed.

2.2.1.1 Hot-Press Bonding

A cuprous oxide coated copper sheet in contact

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TABLE 1

A COMPARISON OF METHODS OF CERAMIC-TO-METAL JOINING

METHOD	CLASSIFICATION *	SPECIAL PROCESSING CONDITIONS **	IMPORTANT JOINT PROPERTIES	GENERAL COMMENTS ON USE
(1) Hot-Press Bonding	One-Step, Solid Phase	Medium temperature pressing in neutral or reducing atmosphere	Vacuum Tight, Low Strengths	Experimental, Limited Shapes
(2) Graded-Powder Bonding	Two-Step, Solid Phase	Cold compacting, medium to high temperature sintering in reducing atmosphere	Vacuum Tight, Usually Low Strength	Experimental, Limited Material Combinations
(3) Gas-Pressure Bonding	One-Step, Solid Phase	High temperature pressing in autoclave	Vacuum Tight, Strength Unknown	Experimental, Complex Precise Shapes
(4) Active-Metal Brazing	One- or Two-Step, Liquid Phase	Medium to high temperature firing in high vacuum	Vacuum Tight, High Strength	Commercial, Limited by Process Sensitivity
(5) Electron-Beam Welding	One-Step, Liquid Phase	Controlled vacuum fusion by an intense electron beam	Susceptible to Massive Cracking	Experimental, Small Joints Only
(6) Glass Soldering	One-Step, Liquid Phase	Low to medium temperature firing in a slightly oxidizing atmosphere	Vacuum Tight, Strength Limited by Glass	Commercial, Low Temperature Applications
(7) Ceramic Brazing	Two-Step, Liquid Phase	High temperature firing in a neutral or reducing atmosphere	High Temperature, Strength and Vacuum tightness	Experimental, Limited Materials Selection
(8) InSitu Ceramic Firing	Two-Step, Liquid Phase	Cold compacting, medium temperature sintering in a oxidizing or reducing atmosphere	Shrinkage sometimes causes leaks and weakness	Experimental, Limited to One Ceramic Composition
(9) InSitu Glass Devitrifying	Two-Step, Liquid Phase	Medium temperature firing in an oxidizing or reducing atmosphere	Properties depend on amount and composition of crystallized phase	Developmental, Possible Wide Applications
(10) Refractory-Metal Powder Coating	Multi-Step, Metallizing	Powder Deposition, high temperature firing in a slightly oxidizing atmosphere, plating	Similar to (4)	Widely used versatility in shapes and materials
(11) Metal/Glass Powder Coating	Two-Step, Metallizing	Powder Deposition, low to medium temperature firing	Usually Not Vacuum Tight, Low Strength	Widely used, versatile, low cost
(12) Metal/Metal-Oxide Powder Coating	Multi-Step, Metallizing	Powder Deposition, medium temperature firing in an oxidizing followed by reducing atmosphere	Similar to (11)	Commercial, Limited Material Combinations
(13) Refractory-Metal-Oxide Powder Coating	Multi-Step, Metallizing	Powder Deposition, medium temperature firing in a reducing atmosphere	Similar to (4)	Developmental, Could Replace (10)
(14) Refractory-Metal Salt Coating	Multi-Step, Metallizing	Salt Deposition from solution, medium temperature firing in a reducing atmosphere, plating, grinding	Similar to (4)	Commercial, Could Replace (10)
(15) Condensed Vapor Coating	Two-Step, Metallizing	Masking, high temperature vaporizing	Similar to (4)	Development, Limited to Certain Shapes Could Replace (10)

* Number of steps does not include parts processing, assembly, metal-to-metallize joining or disassembly

** Low Temperature = $< 450°C$
Medium Temperature = $> 450°C$; $< 1250°C$
High Temperature = $> 1250°C$

with steatite ceramic is held under 3000 psi pressure for 10 seconds at 1000°C in pure nitrogen or hydrogen.[6] Vacuum tight joints are claimed possible by this method. No strength values for the seal were reported but extrapolation of data to the parameters of fabrication indicates tensile strengths of 4100 psi. No known commercial application of this method has been pursued.

2.2.1.2 Graded-Powder Bonding

A ceramic-to-metal joint is formed by pressing together layers of ceramic powder and metal powder and sintering the composite.[10,11,12] The layers can be formed with pure ceramic and pure metal components or may be graded between pure ceramic on one end, through layers of high ceramic-low metal, equal ceramic and metal, and low ceramic-high metal to pure metal. Vacuum tightness has been shown to be possible with this method.[11] No information is available on the strength of such a structure. This type of joint is not manufactured on a commercial basis.

2.2.1.3 Gas-Pressure Bonding

The components to be bonded are fabricated to final size and assembled in a disposable thin-walled metal container. The container is evacuated, sealed, and placed inside a high-pressure gas autoclave and high external gas pressure is exerted at an elevated temperature.[13]

The method is particularly advantageous in the production of complex shapes and in achieving close dimensional control when dissimilar materials are joined. The equipment cost is high and the time at pressure and temperature is long. This process is a development of Battelle Memorial Institute and is not known to be used in any other establishment for ceramic-to-metal joining at the present time. It has been used for the production of flat-plate compartmented fuel cells with significant success.

2.2.2 Liquid Phase Joining

Intimate joining is accomplished through a transient liquid phase. Such a phase could result from a melting of a portion of the metal member or the ceramic member or melting of part or all of an intermediate member. It could also be the result of interactions between any two or all three of the elements.

2.2.2.1 Active-Metal Brazing

Three slightly different methods, with similar end results, typify the general category of active metal seals. In each case the active metal, such as titanium, is added to a braze alloy system which is normally inert and nonwetting on the ceramic in order to promote wetting and/or bonding. The brazing is carried out in a vacuum.

a. __Hydride Method.__[3,5] The joint area of the ceramic is painted with a slurry of the hydride of an active metal (titanium is most commonly used,[3] although zirconium, columbium, and tantalum hydrides have been successfully tested).[5] The metal member is assembled adjacent to the ceramic with a ring or shim ˉ braze material. The assembly is heated in vacuum to reduce the hydride to the pure active metal. The active metal alloys with the braze material and bonds the ceramic and metal members together.

b. __Active-Metal Method.__ The active metal is incorporated with the braze material, either as an alloy or as the core of a braze material.[5,14,15] During brazing, the molten braze material dissolves enough of the reactive metal to wet the ceramic and create a strong bond.

c. __Active-Alloy Method.__ The active alloy is used as a shim between the ceramic and a metal member.[8,16] The metal member must form a molten alloy with the active metal. The active metal may also be used as the structural metal part of the joint, in which case the alloying metal shim is placed between the active metal part and the ceramic.

The active metal method of joining ceramics to metals is widely used in research and production for reliable joining in both hermetic and nonhermetic applications. Its main advantage is in its simplicity. The hydride process has largely been supplanted by the active alloy process which requires only the assembly and jigging of pre-cleaned parts and a single vacuum firing at 10^{-4} to 10^{-5} torr. The disadvantages stem from the close control of processing required and the need for vacuum firing. Time and temperature during processing must be closely controlled by visual observation to prevent overrun of the braze materials onto unwanted areas. The proportions of active metal to alloying metal must be selected within a narrow range to prevent brittle alloy formation. The requirement of vacuum processing precludes the practicability of a continuous production method at the present time. Continuous vacuum furnaces are available but their present high cost obviates their use for this application. A consensus of opinion accords the strength of an active metal joint a slightly lower value than a joint made with refractory metal coatings (discussed under section 2.2.3.1), although no direct comparisons of the two types of sealing methods are known to exist.

2.2.2.2 Electron-Beam Welding

Ceramic and metal parts are fused together directly under a high intensity focused beam of electrons. This method has been investigated with only limited success. Tab welding to micromodule substrates has been shown to be feasible[17] but welds larger than spot welds are susceptible to massive cracking.

2.2.2.3 Glass Soldering

Ceramics are joined to metal through an intermediate

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layer of glass.[18] Such a joint has an advantage over the glass-metal counterpart since the ceramic member, which is not melted during the sealing operation, will provide dimensional control to the structure. The maximum operating temperature and strength of the assembly, however, will be limited by the softening point and tensile weakness of the glass.

2.2.2.4 Ceramic Brazing

The ceramic is fused to a metal member by melting a suitable oxide eutectic between the mating parts.[19] This process is somewhat specialized in that its greatest usefulness is for joints which must withstand service temperatures above 1500°C. The ceramic may be coated with a cermet composition before fusion or may be joined directly to a metal with the eutectic composition. No effort beyond research and development has been expended on this method but the limited results have been impressive. One 99% alumina has been sealed successfully to tantalum, niobium, molybdenum, and tungsten with an alumina-yttria eutectic fusion. Alumina-molybdenum butt seals have withstood fifteen ninety-minute thermal cycles between 500° and 1500°C and remained vacuum tight. A similar seal remained vacuum tight after 1000 hours at 1300°C.

2.2.2.5 In Situ Ceramic Firing

A eutectic of manganese pyrophosphate and magnesium oxide is used as a binder for magnesium oxide and as a sealant for metal conductors. The eutectic is combined with MgO in the ratio of 30:70, is pressed around a metal pin and is sintered at 1180°C for 30 minutes to form a vacuum tight joint. The sintering can be carried out in air, argon, and vacuum.[20]

This method of joining is still in the development stage, although the feasibility of the method has been proven. Further work is contemplated with BeO replacing MgO. It provides a truly one-step joining method, in that the seal is made simultaneously with the sintering of the ceramic body. Nickel-iron alloys, stainless steel, and platinum seals have been accomplished. Because of the firing shrinkage of the ceramic body, joints with metal on the outside circumference of the ceramic cannot be accomplished with the initial pressing and sintering. Such seals can be effected in a subsequent operation by coating the interface between ceramic and metal with the eutectic composition, assembling, and refiring.

2.2.2.6 In Situ Glass Devitrifying

Joints are made by conventional glass-to-metal seal manufacturing methods. The completed assembly is heat treated to a predetermined temperature-time schedule, at which point nucleation and crystallization of the glass occurs.[21,22] Emrich[23] has provided a comprehensive, up-to-date review of devitrified ceramics which includes a historical introduction, a review of the phenomena of nucleation and crystal growth, an appraisal of the state-of-the-art and an extensive bibliography.

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The potential advantages of such a system of p-
ducing ceramic-to-metal joints are many. Manufacturing processes, using
conventional glass working equipment, would be highly automated and the unit
cost could be expected to be much lower than conventional ceramic-metal joints.
Physical and electrical properties, particularly thermal expansion coeffi-
cients, could be varied over a wide range and closely controlled to match
requirements. One crystallized product is claimed to be stable in reducing
atmospheres, which would permit subsequent assembly brazing operations.[21]
The process is not known to be in commercial use in this country.

2.2.3 Metallizing

A thin metal layer is applied to the ceramic member via a
solid, liquid, or gas phase. A metal member can be attached to the metal
layer in a subsequent operation by various metal-to-metal joining methods.

2.2.3.1 Refractory-Metal Powder Coating

Refractory metal powders are mixed with reactive
powders to form a paste or suspension. This is applied in a pattern to a
ceramic and then sintered at a high temperature in a controlled atmosphere.
The resulting conductive layer is electroplated with an easily wettable
metal and the electroplate layer is sintered. The metallized ceramic can
then be brazed or soldered to a metal member.[1,4] This procedure is the
most widely used in the industry today. Pulfrich set down the basic param-
eters for this process in his patent.[1] These parameters are valid today
in spite of the vast modifications and improvements to the method. A high
level of strength and vacuum tightness can be achieved by the sintered metal
process and this method of joining is not critically sensitive to processing
variables when compared to the active metal process. An uninterrupted, con-
tinuous process is possible and is, in fact, practiced where volume require-
ments dictate. Automation has been successfully introduced into some steps
of manufacture.[24] The method, however, is a multi-step operation requiring
several long atmosphere firing operations. The initial sintering of the
refractory metal coating to the ceramic requires a high temperature, usually
beyond the range of the conventional brazing furnace.

2.2.3.2 Metal/Glass/Powder Coating

A finely divided mixture of metal powders and glass
frits, suspended in an organic vehicle, is applied to the ceramic and fired
to cause adherence of the glass to the metal powder and the ceramic. The
metal member is subsequently soft soldered to the exposed metal powder layer.[25]

This process is usually used in non-vacuum tight
applications where requirements for strength and temperature capabilities
are not high but where low cost per unit is a factor. It is widely used for
the attachment of stand-off insulators between components in electrical
systems and for attaching lead tabs on insulating surfaces.

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2.2.3.3 Metal/Metal-Oxide Powder Coating

Finely divided silver and/or copper and the oxide of copper, suspended in a vehicle, are applied to a ceramic and air fired to drive off the vehicles and cause chemical combination of the metal oxide and the ceramic. The coated ceramic is then reduction fired to produce a pure metal coating.[26] This process is used in the same applications as metal powders in glass frits (section 2.2.3.2).

2.2.3.4 Refractory-Metal Salt Coating

Ceramics are immersed in a solution of a refractory metal salt. After drying, the pieces are sintered so that the metal salt is reduced to metal which bonds to the ceramic leaving a thin, adherent layer of metal on the surface of the ceramic. This metal layer is plated and the ceramic-metal joint can be made by brazing. The sintered metal layer must be ground off the areas in which insulation is desirable.[27,28]

This method was originally developed and has been used for ceramic-metal tube programs. Vacuum tight joints can be achieved by this method and strengths are sufficient for the application. This process is advantageous in metallizing the inside diameter of small lead-through holes.

2.2.3.5 Refractory-Metal-Oxide Powder Coating

This process is similar to the Refractory-Metal powder Coatings. The refractory metals are applied as oxides instead of in elemental form. Lower sintering temperatures can be used.[29]

The use of refractory metal oxides in place of the elemental metal is not new.[30,31,32] Its desirability lies in the possibility of a low temperature firing of the metal coating, nickel coating, and braze material in a single operation to effect a seal. The degree of success has not been sufficient to make noticeable inroads into the higher temperature, multi-fire method.

2.2.3.6 Condensed Vapor Coating

A very thin metallic coating is applied by the volatilization of a metal and its deposition onto the ceramic.[33,34] Many different methods of volatilizing the metal are possible which include:

1) Heating of a metal beyond its boiling point.
2) Breakdown of a compound to yield elemental metal.
3) Exploding wire or foil techniques.
4) Ion bombardment.
5) Plasma spray coating.

Much interest is being shown in this method of metallizing ceramics. A very thin, tenacious coating is possible without excessively heating the ceramic member. By masking techniques, the area of coating can be controlled. The process can be accomplished with relatively inexpensive equipment in a short time operation.

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2.2.4 Metal to Metallized Layer Joining

Joining of the metal member to the metallized ceramic is usually accomplished by conventional brazing or soldering. However, other techniques have been developed or applied for specialized applications to effect the final joint between ceramic and metal. Diffusion bonding, ultrasonic joining, and electroforming have been used for this purpose.

2.2.4.1 Diffusion Bonding

A metal and a metallized ceramic, with or without an interlayer of another metal, are pressed together below the melting temperature of any of the components but above their recrystallization temperature. The combination of temperature, pressure, and time promote plastic deformation of the metals and intimate contact of the surfaces.[12,35] This process can be applied to high temperature service joints which can be formed at temperatures below the melting point of any of the components.

2.2.4.2 Ultrasonic Joining

A metal and a metallized ceramic are joined by introducing high-frequency vibratory energy into the overlapping pieces. A brief transmission of this energy into the work-piece under moderately low static force will produce a sound metallurgical bond.

This method of joining has been used in the sealing of transistor packages in an application in which the presence of a flux was detrimental to the operation of the device.[36] It consisted of the soldering of a metallized ceramic to a brass cap with an interlayer of solder.

2.2.4.3 Electroforming

The metal and metallized ceramic parts are stacked on a jig and, after electrical contact is made to the surfaces to be joined, the assembly is electroplated for a period of time sufficient to bridge the gap between the two parts.[37] A method is thus provided which will allow the joining together of components at room temperature. With proper processing, a coating 0.008 inches thick can be built up in 24 hours. The joint is claimed to be vacuum tight. The assembly can subsequently be baked and outgassed.

2.3 Future Advances

The present high cost of ceramic-to-metal joints, particularly in comparison with glass-to-metal seals for electrical/electronic applications, is probably the biggest factor in a continuing search for manufacturing process simplification that will result in a reliable ceramic-to-metal joint. It is the policy of the device manufacturer to employ glass-to-metal seals up to the limits of their usefulness rather than accept the considerably higher cost of ceramic-to-metal seals to attain higher reliability. Wider substitution of ceramic for glass will occur in proportion to the reduction

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of the cost difference betwe.n the two joint types. Future advances, based on cost reduction and the resultant wider use, can be expected from the following areas:

1) Improvement and simplification of existing processes.
2) Development of research techniques to useable production methods.

In the first area, improvement and processing simplification will have to be significant. Methods of vapor depositing metallizing coatings on ceramics are being studied and it is probable that a production method will be realized in the near future. The Signal Corps contract to investigate low temperature refractory metal-to-ceramic seals[29] may result in a one-fire method of joining with refractory metal coatings. The use of glass which devitrifies to a stable ceramic[21] has received sparse attention in ratio to its possibilities for a low cost ceramic-to-metal joint. A reliable active metal seal which can be accomplished in a non-vacuum atmosphere and which is not sensitive to minor processing variations will result in a product that will be more economically competitive with glass-to-metal seals. Known methods of joining which were disclosed in the literature in the early 1950's, such as reported by Wellinger[6] and Bender,[15] but which are not being utilized today can be re-examined in the light of present technology. It is possible that, with some modifications, useable processes can be realized.

Cost reduction has been stressed in the foregoing paragraphs. Quality improvement is considered of lesser importance for wider acceptance of conventional ceramic-to-metal joints. Reliable joints, with ample temperature and strength characteristics for most electrical and electronic applications, are attainable with the present methods of manufacture. In aerospace applications, where quality and reliability are considered of primary importance, the greatest advances can be expected in improved materials and quality control, rather than in improved joining methods.

3. Design and Materials Considerations

3.1 Design

3.1.1. General

The design of ceramic-to-metal assemblies has been reviewed periodically in trade journals. Cronin[38] in 1956 traced the development of ceramic-to-metal seals and described typical joints in terms of materials, geometry, and brazing practice. He described specific tests for the evaluation of ceramics and the measurement of bond strength and outlined the stress-strain relationship of the completed joint in terms of thermal expansion, heat conductivity, and thermal history of the assembled components. Van Der Beck[39] in 1959 and Larsen[40] in 1961 laid down some general rules for the design of ceramic-to-metal joints. These three references combined with a review of the stress-strain relationships in glass-to-metal seals as set forth by Hull and Berger[41] and Monack[42] will provide some background for the design of ceramic-to-metal joints.

In the area of more specific design information, several investigations are worthy of note as examples of the scientific approach to proper design. Cole and Inge[43] predicted stresses in a ceramic-to-metal brazed joint from theoretical considerations and, in a continuation study, Inge and Swanson[44] devised a method of experimental verification of the stresses. Wilson and Long,[45] in establishing design parameters for the mechanical attachment of ceramic radomes, substituted annealed glass for the ceramic member in study systems and by photoelastic inspection of the strains set up under loading conditions, arrived at designs which induced the lowest stress concentrations. Lee and Lelo[46,47] investigated the problem of excessive thermal stresses developed in the junction of a refractory metal disc sealed to an alumina cylinder. By mathematical analysis they were able to reduce the resulting shearing stresses to one-fifth of the original amount with modified joint configurations. Much more of such investigative and analytical work can profitably be initiated in the area of proper design of ceramic-to-metal joining.

3.2 Materials

3.2.1 Ceramics

The raw materials for ceramic products have historically been impure, crude, and inexpensive. The clays and sands, the limestones and feldspars traditionally used are available in quantity, widely distributed and easily obtainable. To assure a degree of property consistency, clays were mined from guarded secret areas or secret minerals were added to the raw materials batch. Thus, the early history of ceramics resulted in a technology based on impure materials, proprietary knowledge, and tradition.

This philosophy existed to some extent in the period when ceramic-to-metal joining had its beginning. It has only slowly given way to the proven advantages and needs for pure, consistent materials and

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meaningful, reproducible property data. The ceramic formulations used by Pulfrich and Magner[1] in the 1930's were compounded of major percentages of kaolin (china clay) and soapstone with the resultant loss of property control because of composition inconsistency. Pulfrich[48] described the tests necessary to assure an acceptable body as follows:

> "....the (quantitative) analysis gives an approximate picture of the suitability of the raw material. In order to ascertain an exact survey of the suitability of the raw material it is necessary in each case to prepare a trial sample, compress it into ceramic bodies and bake them. A few of these specimens are metallized and soldered in order to test the adhesive strength; others are tested for bonding strength, for their electrical properties such as insulating and dielectric constant and loss factors. It is only after these tests that the suitability of a given raw material can be decided upon."

After the success of the Telefunken ceramic-to-metal tubes was disclosed in this country, several investigative studies were initiated to duplicate or improve the process. The available bodies were the forsterites and steatites which proved to have poor thermal shock resistance. In the early 1950's, the high alumina compositions which had been developed during World War II for spark plug bodies were substituted as the ceramic members. The resulting assemblies were found to have far superior thermal shock resistance.

The alumina bodies that were utilized in ceramic-to-metal joints ten years ago were poorly defined in terms of today's purity levels. Hynes[49] reviewed the requirements, fabrication and control of alumina bodies in 1956 and noted the following concerning the additives which were incorporated into the alumina bodies at that time:

> "Review of the existing literature, particularly that pertaining to spark plugs, indicates that a great variety of materials have been added with alumina in body formulation. Some of these are materials of the sillimanite group, various kinds of clay, talcs and other silica bearing minerals, alkaline earth oxides, phosphates, oxides of chromium, zirconium, titanium and a host of other metallic oxides."

> "Ceramic-metal seal bodies generally may be classed as glass-bonded alumina bodies. Thus added to silica are sufficient alkaline earth materials to give a viscous glass phase. In addition, materials may be added to control grain growth."

The recent trend has been toward fundamental improvements in ceramic bodies. The severe environments of the space age have nurtured a need for more reliable materials, optimization of properties, and basic

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information on material capabilities. The increased need for greater reliability of space electronics has added emphasis to the program for improvement. The investigations of Cole and Sommer,[50] of Floyd[51,52] and Reed, et al[53] have made it apparent that the effects of the minor ingredients are not of only minor importance. The fluxing constituents, the firing history of the body, the metallizing compositions and sintering phase, and recrystallization processes must be investigated. The effects of these parameters have made it apparent that the manufacture of ceramic bodies requires close control at every step, from the analysis of the raw materials to the final finished product tests. Clays, soapstones and other minerals are being replaced by pure chemicals in the batches.[54] Firing schedules are being programmed and kilns are being instrumented to a greater degree to assure the proper grain size and crystal shape of the finished body. Amount and homogeneity of glassy phase is being controlled and voids are decreasing in size and number.

New materials are being investigated and new bodies are being produced that can find application as ceramic-metal joints for space, electronics and industrial uses. Carbides, nitrides, sulfides, and borides have joined the oxides for refractory applications.[55] The properties of most of the compounds in these groups have not been extensively examined. Nevertheless, it is known that among these ceramics are materials with the highest known melting points, (well in excess of one hundred different ceramics melt above 2000°C). Many retain useable strength at high temperatures and many are oxidation resistant for possible use in high temperature ceramic-metal assemblies. The unique electrical, thermal, and mechanical properties of boron nitride are of such attraction that several investigative projects have been initiated to explore its manufacture and applications.[55,56,57] Silicon carbide, which in the past has been used primarily as grinding and cutting grains and as resistance heating elements, is gaining new prominence in satellite heat shields and for microwave attenuation.[55] The rare earth oxides have been produced in high purity bodies and exhibit many desirable properties such as refractoriness, chemical stability, good electrical resistance, low thermal expansion, and resistance to nuclear radiation effects. Their present high cost can be expected to decrease with improved production techniques so that economic use can be achieved in ceramic-metal components. The combination of high electrical resistivity, high thermal conductivity, chemical stability and refractoriness of high purity beryllia have established it as a competitor to the high alumina ceramics in some ceramic-to-metal applications.[58] The properties of stabilized zirconia, which has good thermal shock resistance and melts above 2500°C are being studied for high-temperature joint applications.[59]

For most ceramic materials, a concentrated effort is required in the more precise reporting of manufacturers' property data. At the present time, a committee of fabricators and users is working through the American Society for Testing and Materials to provide a uniform, expanded specification for ceramics. Still, in the field of ceramic-to-metal joining, the technology continues to advance at a far faster pace than the science because proprietary

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methods and material formulations persist. Reed[60] noted the following effects of this philosophy at the beginning of an extensive study of the basic mechanisms of adherence in ceramic-metal seals and the problems connected with the use of ceramic-to-metal seals in electron tubes:

> "In any basic program it is desirable to obtain as full an understanding of the materials and processes used as possible. This is not feasible with commercial ceramics due to proprietary materials and processes. This casts no reflection on a particular ceramic supplier. The industry at this time guards its formulations and processes with great care."

Lynch and Krochmal[61] noted that what they term the ceramic 'science' has only recently and not too seriously become concerned with impurity levels of ceramic materials and they find it not surprising that this ceramic 'science' is at least a generation behind that of metals.

Frequent references to the lack or inadequacy of ceramic property data are made in the literature. Shook[62] states that it has long been recognized that the available data on the mechanical properties of brittle materials are far from adequate for most critical design purposes. McKellar,[63] writing on Material Properties Affecting Thermal Design in the Space Materials Handbook, commented that thermophysical property data are either unavailable or questionable for many ceramic materials. Chapin[64] found that the amount of radiation effects information on ceramic tube envelopes was not sufficient for a reliable comparison between ceramics and glass.

As an attempt to overcome these deficiencies, a Mechanical Property Survey of Refractory Nonmetallic Crystalline Materials and Intermetallic Compounds[65] was published and was updated and revised in 1964 under the title of Refractory Ceramics for Aerospace.[66] The limitations of the existing data were recognized in the revised work:

> "Despite the large amount of published ceramic property data, there are relatively few data available of the type and quality required for design. This results from a lack of extensive testing of a given ceramic and also from the sensitivity of the properties of ceramics to fabrication and test techniques, so that comparisons of data from various sources are difficult. These difficulties are intensified when the design engineer is not familiar with ceramic technology."

> "...Because the quality of much of the data presently available is open to question it is unrealistic at this time to consider the preparation of an actual design handbook."

The property data presented in the <u>Refractory Ceramics for Aerospace</u> and collected by the Electronic Properties Information Center[67] and the Ceramics and Graphite Information Center[68] should logically be compiled as a ceramics handbook. The expansion of the services of these two agencies to provide more current information and to report the results of current research and development in the ceramic field is desirable. Greater publicity on their existence and function, and the amount and availability of the data which they are collecting is needed.

3.2.2 Metals

In general, it can be said that metals, whether elemental or alloyed, can be produced in higher purity with more uniformity of properties, to give a more reliable product than ceramics. Property data is more complete and more readily available for metals than for ceramics. This situation is the logical result of long standing demand and need in the fields of metal use as compared to the relatively new requirements for ultra-pure ceramic materials.

Physical property data of metals and alloys have been tabulated in several references[69,70,71] and volumes have been written on the properties of the individual metallic elements and their principal alloys. Typical metal data which is of interest to the designer of a ceramic-to-metal joint includes:

Coefficient of thermal expansion (room temperature to joining temperature).

Chemical reactivity in high temperature gaseous atmospheres.

Thermal conductivity.

Ductility (room temperature to use temperature).

Melting point and phase relations with braze metals.

Mechanical strength (room temperature to use temperature).

Magnetic properties, including Curie point.

Nuclear radiation effects.

Cryogenic temperature effects.

Vapor pressure at use and brazing temperatures.

Such data are generally available in handbooks or as data sheets supplied by metal fabricators. Notable exceptions to this are high temperature thermal expansion and mechanical strength. Values above 1000°C are usually obtained by extrapolation.

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The Defense Metals Information Center[72] is engaged in the collection, compilation, and dissemination of basic data and up-to-date information on metal properties and the results of current metals research. The periodic reports and memoranda on metal properties, fabricating and processing methods, and industrial surveys are supplemented by periodically issued news sheets which review recent developments in the metals industries. The reports of DMIC are available to Government agencies, Government contractors, subcontractors, and their suppliers on a no-charge basis and to others for a nominal fee from the Clearinghouse for Federal Scientific and Technical Information, U.S. Department of Commerce.

Although the dissemination of information for metals has been more thorough than for ceramics, many needs exist for improved properties of metals, especially in respect to ceramic-metal joining and applications. An increase in high temperature (above 1000°C) strength and greater oxidation resistance is being investigated for aerospace and missile re-entry applications. Less is known of the need for oxidation resistance of metals for electronic applications. Higher bake-out temperatures for microwave tubes will increase the service life by lessening the possibility of tube outgassing during use. The present method of high temperature processing made possible with ceramic-to-metal vacuum seals requires a neutral or reducing atmosphere for periods of forty-eight hours and longer. Competitive pricing often precludes the equipment and gas consumption necessary for this step, with the result that the higher outgassing temperatures are not used. Oxidation resistance for tube materials: copper, nickel, molybdenum, and the nickel-iron alloys in the 700-900°C range is needed by the electron tube industry. Periodically, the need arises for a low cost, easily formable metal which is non-magnetic and has a coefficient of thermal expansion in the range of 7.0 to 8.0 x 10^{-6} inches per inch per degree centigrade. The need for a non-magnetic sealing alloy, inert to 30 to 40 percent potassium hydroxide at 50°C has been expressed in a cadmium-silver oxide battery project.[73]

3.2.3 Accessory Materials

In addition to the structural ceramic and metal components which are joined, accessory materials are usually necessary to effect the joint. In many of the more common ceramic-to-metal joining methods, the ceramic surface to be joined is first metallized with a metal-containing slurry, solution or vapor. Such a metallized layer is usually plated to provide a surface which is more easily joined to the metal part by a subsequent metal-metal joining operation such as brazing or soldering.

3.2.3.1 Metallizing

Metallizing slurries containing metal powder, a binder and a vehicle are painted, sprayed or in some other manner evenly deposited on the ceramic and then dried and sintered. The formulation of metallizing mixtures is the least scientific step is the ceramic-to-metal joining process. The composition of metallizing mixtures and the processing

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of slurries is usually considered of a proprietary nature. Cole, et al[50] listed and tested approximately two hundred metallizing compositions. Unfortunately, however, the scope of the work limited the number and the detail of evaluation tests on each formulation. Some attempt was made to categorize the various compositions but a detailed explanation of the function of each component was lacking. The metallizing of oxide ceramics has been the subject of a comprehensive study by Reed, et al.[74,75] The process has been treated from both a practical and a theoretical viewpoint and has been reported in detailed chronological order, beginning with the functions of the metallizing suspension components and following each step of the process in detail to an examination of the effects of various braze materials on the adherent metal layer.

The proper preparation of metallizing slurries is a complicated task which requires specialized knowledge of comminution mechanisms, the characteristics of sols, gels, slurries and dispersions and an ample background in the chemical and physical properties of organic vehicles. This specialized knowledge and the proper equipment is usually not readily available to the average ceramic-to-metal joining group. That usable metallizing mixtures can be produced with only a part of the specialized knowledge and equipment attests to the fact that most of these systems are not greatly sensitive to minor variations for many applications. For those critical applications in which the last measure of strength and reliability is necessary, it is possible to purchase manufactured metallizing slurries. Prepared decals and tapes[76] are available in standard or specialized formulations. It is also possible to have mixtures of metal powders milled and combined with the proper organic vehicles on a commercial service basis.

Two newer techniques for metallizing which do not use metal in powder form are solution metallizing and vapor deposition. Both of these methods can produce a metal coating on all surfaces of the ceramic unless certain areas are previously masked. Lithium molybdate dissolved in water was first used for solution metallizing[27] but it has been shown that a number of refractory metal compounds in a variety of solvents can be successfully employed.[29] All of these compounds dissociate at a relatively low temperature and leave an adherent metal layer on the ceramic. Vapor deposited coatings, on the other hand, can be achieved by using either metal compounds or pure metal. In the case of the metal compound, dissociation must take place on the surface of ceramic producing an adherent film of metal, whereas metal is deposited directly by vaporizing the required metal adjacent to the ceramic surface. A wide variety of metals can be deposited by this method but the evaporating and condensing conditions must be controlled for each system. Both solution metallizing and vapor deposition are sometimes followed by a grinding operation to remove metal from unwanted areas prior to plating or joining.

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3.2.3.2 Platings and Coatings

Because the metallizing layer usually contains high concentrations of materials which are difficult to wet during conventional brazing or soldering, a metal plating, usually nickel or copper, is first applied to the metallized surface of the ceramic. The application of the plated layer is sometimes preceded by a brushing, buffing, or tumbling operation which serves to polish the metal surface and remove any gross contamination caused by the metallizing step. The plating can be applied by electrodeposition techniques. Johnson and Cheatham have detailed typical electroplating procedures and recommended electroplating bath compositions as an appendix to a Manual of Metal-to-Ceramic Sealing Techniques.[77] Coatings can also be applied non-electrolytically by painting, spraying, or screening fine-mesh metal powders onto the metallized surface. Nickel oxide or nickel powders are usually employed because they are obtainable in very fine particle sizes. The coatings are sintered to improve the metal-to-metal bonds and to outgas the exposed metal layer.

3.2.3.3 Braze Materials

A listing of braze materials, their flow and melting temperatures, pertinent notes on applications, alloy compositions, and suppliers has been published in Kohl's "Materials and Techniques for Electron Tubes."[78] Recent investigations[79,80,81,82] in this field have added materials which should be included in a revised listing. Other property data such as thermal expansion of braze alloys is difficult to obtain. Although the effects of expansion coefficient and ductility are often considered minor because of the layer thinness, the frequency of joint failures [9,83] caused by braze rupture attest that this information is important, and should be more thoroughly reported in the literature.

Braze materials can be purchased in several grades of purity. The utilization of vacuum tube grade is imperative if high vapor pressure metals, present in technical grade materials, will be detrimental to the application of the joint in the completed system. The more commonly used braze materials may be purchased off the shelf as carefully dimensioned rings, shims, and washers and also as a cladding on various metal substrates.[27]

The braze materials used in active-metal brazing are available in a variety of forms. Pre-alloyed braze components can be purchased, for example, as wire, foil or powder which contain controlled amounts of titanium or zirconium additives. Similarly, braze clad active metals can be purchased where the amount of core material in the wire, foil or powder is specified.

3.2.4 Materials Considerations for the Future

The traditional concepts that certain amounts of impurities are a requirement for the fabrication of a reliable ceramic body, which were accepted in the early days of the joining industry, must be modified to gain wider acceptance and confidence for ceramic-to-metal joints. It was not until recently, under the pressure of aerospace requirements, that ceramic-to-metal joints were investigated, fabricated, and used with the care required

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for a brittle material. In view of the fact that ceramics are a brittle material, the most pressing need today is the measurement, collection and publication of reliable property data. The dissemination of these data in handbook form, such that seal designers, producers, and users can use effectively, will provide the basic information which is needed for creative advances.

Materials problems of metals, specifically in relation to ceramic-to-metal joining, have not been as serious as those of ceramics. Although some metals are described as lacking ductility, their brittleness does not approach that of ceramics. For this reason and because the need for pure metals far predated the newly emergent need for purity in ceramic materials, information on metals properties is more available and more reliable than that of ceramics. However, improvement in properties is still needed to extend the applications of metals, especially where there is a requirement for high temperature strength and oxidation resistance. A ceramic-metal assembly must be considered as a package from a materials standpoint. A weakness in any one component, whether a major part or an accessory material will be detrimental to the assembly as a whole. Any improvement in joining techniques related to materials will reflect an improvement in the materials and the assembly. The attainment of greater reliability in ceramic-to-metal joints will be hastened with the availability of reliable property data on all the components and their interrelation in the whole seal as surely as it is being hindered by this lack of information today.

4. Equipment

The early history of the ceramic-to-metal joining industry was typified by the utilization, with adaptation and modification, of the existing equipment which was used by chemical laboratories, machine shops, metal processing operations, material handling groups, and other areas. Assuming that the joining process starts with shaped ceramic and metal parts, there is still very little unique ceramic-to-metal joining equipment per se. (See Table 2) If, as is quite often the case, the ceramic-to-metal assembly is being produced to supply in-house requirements for a larger assembly, the more elaborate and expensive units of equipment will be shared with other disciplines. Chemical cleaning and plating facilities which serve the whole operation will be utilized for ceramic processing. The metal brightening, outgassing, and annealing furnaces will be used for sintering the metallized and plated ceramics. Conventional ball mills will be operated with a charge of metallizing slurry. Standard brazing furnaces will be used universally for metal-to-metal joints or ceramic-to-metal counterparts.

Although the system of adaption or sharing is economical as far as capital equipment outlay is concerned, there are certain inherent dangers. Experience in cleaning, plating, and atmosphere firing of metal parts cannot be automatically applied to the brittle ceramic materials. Consideration of the effects of heat shock and mechanical strength of the non-metals is of first level importance, particularly when the completed joint is being processed. Utilization of equipment which is inadequate for the application can be expected to result in a substandard product or an overextension of the capabilities of the apparatus. For example, attempts to use an atmosphere furnace designed for 1250°C operation to sinter a metallizing layer which requires a 1450°C temperature will obviously result in underfiring of the coated layer or drastically shortening the life of the furnace. With dual purpose sharing of facilities, cross-contamination is an ever-present possibility. Some of the adaptations and modifications have been applied with considerable ingenuity; others with insufficient forethought. As a general rule, attempts at automation and specialized equipment have been limited to one-of-a-kind labor saving devices which are built with in-house facilities to guard against duplication.

The vacuum or atmosphere furnaces represent the largest capital expenditure for a ceramic-metal joining group. It is only recently that atmosphere furnaces have been designed and advertised as ceramic metallizing furnaces. Designs have, in most cases, emphasized proper peak temperatures and controlled preheating and cooling sections. Exemplifying this, a U-shaped furnace has been designed and operated with two intermediate temperature range legs in which nickel coat sintering and brazing can be accomplished, and a high temperature base section in which metallize sintering is effected. The leg portions also act as preheat and cooling sections for the high temperature operation.

The area in which automation has been applied to the greatest extent has been in the application of metallizing coatings. Dip coating machines

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TABLE 2

TYPICAL EQUIPMENT REQUIRED FOR CERAMIC-TO-METAL JOINING

I. INCOMING INSPECTION EQUIPMENT

    A. Physical Testing
        (1) Shape and size
        (2) Density
        (3) Thermal expansion and conductivity
        (4) Visual - macroscopic, dye check; microscopic, structure
    B. Chemical Analysis
    C. Mechanical Testing
        (1) Strength
        (2) Hardness
        (3) Ductility
    D. Electrical Testing
        (1) Resistance
        (2) Dielectric strength

II. MATERIAL PREPARATION EQUIPMENT
    A. Ceramic and Metal
        (1) Degreasing
        (2) Cleaning - chemical, ultrasonic
        (3) Prefiring - medium temperature, air or reducing atmosphere
    B. Metallizing Slurries
        (1) Analyzing particle size
        (2) Comminution - ball or rod mill
        (3) Mixing - mechanical, magnetic
        (4) Measuring viscosity

III. COATING EQUIPMENT
    A. Metallizing
        (1) Applying - brush, spray, silk screen
        (2) Drying - low temperature
        (3) Sintering - high temperature, slightly oxidizing atmosphere
    B. Finishing
        (1) Buffing, tumbling
        (2) Plating - containers, baths: strike, plate, rinse
        (3) Sintering - medium temperature, reducing atmosphere

IV. JOINING EQUIPMENT
    A. Assembling
        (1) Jigging and fixturing
        (2) Automatic handling
    B. Firing - medium temperature, reducing atmosphere

V. OUTGOING INSPECTION EQUIPMENT
    A. Destructive - similar to incoming; inspection depending on application
    B. Nondestructive
        (1) Leak detection
        (2) X-ray and ultrasonic inspection

for uniformly coating all exposed areas of the ceramic, adaptations of silk screen processes, printing presses and decal transfer mechanisms are in use and a metallizing-tape application machine has recently been developed.

Ceramic-to-metal joining equipment has, therefore, been typified by direct utilization of the apparatus and machinery of other disciplines with modifications to fit the requirements of the new processes. Little attempt has been made to view ceramic-to-metal joining equipment as a new field which requires new machinery designed solely and uniquely for the function it will serve. Rather, the processes involved in permanently attaching a metal member to a crystalline ceramic piece have been viewed as an extension of the art of metal-to-metal joining or glass-to-metal joining and as such, the use of the equipment which was developed for these parent areas has in general been considered sufficient when adapted and modified to the new needs. As a matter of economics, however, it is doubtful that extensive development of distinctive equipment for the manufacture of ceramic-to-metal assemblies can be justified in the near future.

5. Test Methods

5.1 Purpose of Testing

There are two general areas into which the purpose of testing can be aligned: the generation of basic property data and the comparison of quality. For the generation of basic property data, testing must be continually oriented toward absolute values. Quality can be compared against a pre-established set of goals (specifications) or between individual products, whether of the same model, different models, or different concepts. Tests for a comparison of quality do not require the precision that is attendant with basic property data investigations. The conditions of tests for quality acceptance are detailed within limits by written specifications which also set the end point limits. Such limits are usually in the nature of minimum and maximum. A comparison between individual products usually results in an approximation of per cent better.

5.2 Methods of Testing Ceramic-to-Metal Joints

Procedures for testing ceramic-to-metal joints are largely adaptations of methods used to test the properties of the individual materials where such methods are applicable. Some procedures have been borrowed from the metallurgical discipline. Very little standardization is in effect, industry-wise, in spite of recognized need and the efforts of such organizations as the American Society for Testing and Materials. In this report, therefore, no attempt will be made to describe individual testing methods in detail. Minor variations will be grouped under the applicable procedures. Mechanical strength testing has been separated into sub-groups but this is no assurance that a described tensile test, for instance, will produce a figure of nearly pure tension, unaffected by substantial torsional, compressive, or shear influences. In some cases, the complexity of the forces acting on a joint during test make the selection of the proper grouping a difficult task.

5.2.1. Mechanical Tests

5.2.1.1 Tensile Strength

Tensile tests measure the resistance to pulling apart where opposite forces are applied perpendicular to the braze face in a direction away from the braze area. The test can be performed in a variety of ways. Direct, opposing forces can be applied,[91] the one component (in the form of a cap) can be pushed off the other component (as a cylinder) by mechanical or fluid pressure,[29,92] or fluid pressure can be applied to the inside of a hollow sphere which is made up of two hemispheres brazed together.[93]

The ASTM tensile test[91] is the most widely used test for measuring mechanical strength of ceramic-metal joints. The test is performed by metallizing and brazing together two pieces of ceramic of a specified size and shape (see Fig. 1), and subjecting the assembly to opposite forces in a direction perpendicular to the braze interface. It has found enough acceptance that it can be referred to as the unofficial standard of

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Parallel to ±0.003"
±0.076 mm

Grind Face
Flat to 0.00025"
0.0064 mm

A

0.093" Flat
2.36 mm

B

1.115" ±.010
28.32 mm ±0.25

0.625" ±.005
15.87 mm ±0.13

10.21 mm ±0.13
0.402" ±.005

7°40" REF.

0.125" R
3.17 mm

0.412"
10.48 mm

C

0.562" REF.
14.27 mm

A — SEAL SURFACE AREA TO BE METALIZED.

B — SURFACE INSCRIBED WITH DATE AS TO CERAMIC
BATCH & FIRING TEMPERATURE.
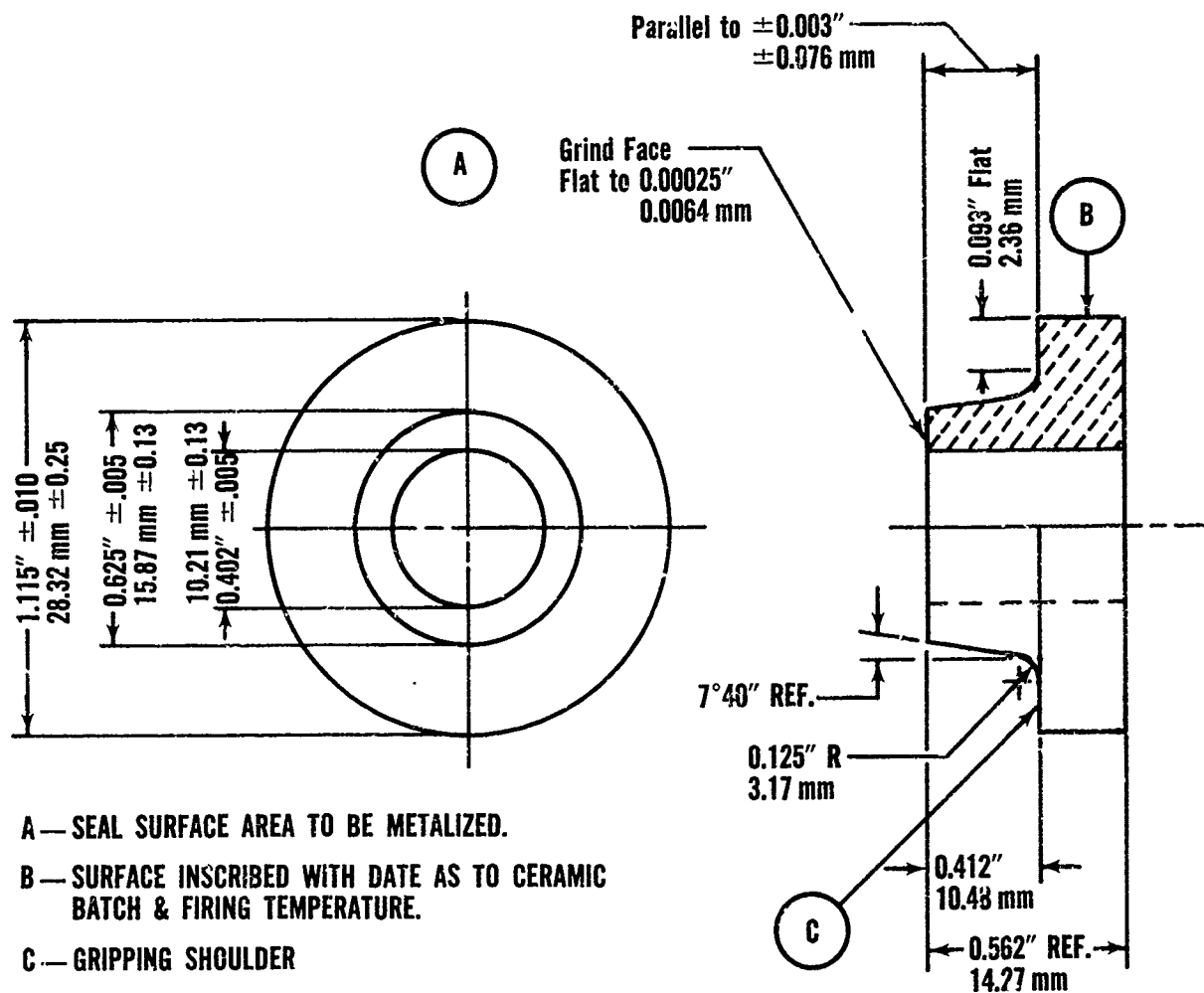
C — GRIPPING SHOULDER

Figure 1. — Tensile Test Piece.

the industry. It is used for inter-industry comparisons of quality and intra-department tests of new processes and material comparisons. As such, very little data are published; nearly all the comparisons or disclosures of strength data are verbally given during discussions of papers presented at technical meetings and symposia. The consensus of opinion (again mostly verbal and not published) is that the ASTM tensile test needs much improvement. Johnson, et al[94] noted the possibility of residual error from this test method as follows:

> "The results of the experiments were masked to a large
> extent by residual error caused by uncontrolled and/or
> unknown variables. The ASTM test vehicle employed in
> the program was apparently the source of the variable."

Shoulder breaks in the ceramic test piece are reported in many cases.[29,32] This condition is sometimes referred to as an indication that the seal was stronger than the ceramic.[95,96] No mention is made of the possibility of gripping devices or misalignment causing localized stress areas at the point of break. Proper alignment, either during the brazing of the test halves or during the tensile test procedure is virtually impossible to attain. The relatively high cost of the test pieces discourages their use for mass tests in numbers that would produce a level of statistical confidence. Since the shape of the test piece is specified, the method cannot be used for direct quality control of production processes.

5.2.1.2 Peel Strength

A peel test[97] is performed by mechanically stripping the metal member from the ceramic. This test is performed by pulling a tabbed metal strip from the surface of a ceramic plate or from the outside diameter of a ceramic cylinder to which it has been brazed.

Peel tests have found favor in production quality testing. The method is easily adaptable to production shapes, requiring only a plane surface to which a metal strip can be joined and later stripped away. The force required to peel the metal strip can be measured with a fair degree of reproducibility by employing a spring scale. The test is frequently used without pull force measurement by viewing the stripped surface and attempting to correlate bond strength with the amount of ceramic which is pulled away. The use of such a non-definitive test (or the related method of simply crushing a seal in a bench vise and examining for adherent ceramic), often results in faulty information. Large pieces of adherent ceramic which, by this test are considered indications of excellent bonding, can actually be evidence of surface flaws, too large a crystal development, excessive glassy phase, or any of a number of defects in the ceramic body or of the processing steps of manufacture of the joint.

5.2.1.3 Flexure Strength (Modulus of Rupture)

Flexure strength is the measure of resistance to failure when a bending moment is applied to the ceramic-metal joint. The components, usually two ceramic members whose length to cross-section ratio is large, are butt-brazed together or butt-brazed to a relatively thin metal

section. Two equal forces are applied in one direction parallel to and equi-distant on each side of the braze face while an opposite force is applied parallel to the braze face at the joint (three point loading);[85] or two equal forces are applied in a direction opposite to the original forces parallel to and equidistant on each side of the braze face but not directly opposite the position of the original forces (four-point loading).[86] The forces are positioned to produce a bending moment at the braze area.

The four-point loading flexure tests are gaining favor for comparison testing of processing and material changes. The first advantage of the method is that the joined sample can be prepared from actual parts used in production. Typically, a joint is made between two ceramic pieces and 0.025 inch square bars are cut from the assembly. After diamond polishing with a 150-grit diamond wheel in a direction parallel to the axis of the part, the parts are tested in flexure.

5.2.1.4 Torsional Strength

Torsional testing is the measurement of the strength of a joint when a twisting load is applied to set up a shearing force at the ceramic-metal interface. A joined assembly is held stationary at one end so that the braze area is free. A rotational force is applied to the other end in a direction parallel to the braze face. Torsional tests of joints are generally performed only when the application will be subjected to severe twisting stresses. The method is sensitive to stress arising from misalign-ment and clamping.[87]

5.2.1.5 Shear Strength

Shear testing is the measure of the force required to cause two contiguous parts of a joint to slide away from each other. Two forces, moving in a plane parallel to the braze face, are applied in opposite directions on opposite sides of the braze interface.[88,89] Alignment and clamping difficulties make the test unpopular. An applied stress which can be considered pure shear is rarely attained.

5.2.1.6 Compressive Strength

Compressive tests determine the resistance to crush-ing forces. Opposite forces are applied perpendicular to the braze face in a direction toward the braze area.[90] Compressive tests are seldom performed on ceramic-to-metal joints. The very high compressive strength of ceramics makes this property a matter of small concern.

5.2.1.7 Mechanical Shock and Vibration Resistance

Mechanical shock and vibration tests are performed to determine the ability of a joint to withstand sudden application of stresses or the continuous application of oscillatory stresses of short periodicity. The joint is clamped to a fixture through which mechanical shock and/or vibratory motion is transmitted. Orientation of the joint in relation

to the direction in which the force is applied is usually specified.[98] Although not strictly within the above definition, centrifuge tests may be considered related because the joint is clamped into a fixture and rotated in a fixed circular orbit at a high rate of speed. Tests in this grouping are usually well detailed in Government specifications for severe service applications.

5.2.2 Impermeability Tests

Impermeability is the measure of the resistance of a joint to the passage of a fluid through the joint. Several different methods of testing for impermeability are in use.

The mass spectrometer leak detector[99,100] is employed for the detection and measurement of small leaks. The joint is sealed to a mass spectrometer tube and the area around the joint is flooded with helium. Flow rate of the helium through a leak will be detected and measured by the mass spectrometer. This method is the most sensitive of leak detection techniques. However, care must be exercised in attaching the assembly to the vacuum port so that a leak in the seal between the instrument and the assembly under test rather than a joint leak will not be indicated. It is very difficult, if not impossible, to pin-point small leaks. Gross leaks tend to flood the instrument and add pump-down time to the tests. Bubble tests[99,101] are used for the location of gross leaks. The joint is immersed in a liquid and a gas is introduced under pressure into the assembly. Bubbling of the gas at the leak location will give a relative indication of the size of the leak. The simplest system in use employs water as the liquid and air as the search gas but systems of liquid ether and hydrogen are claimed to provide a greater sensitivity.

Radioactive tracer gases are employed[100] by enclosing the joint in a system and introducing the gas, under pressure, around the seal. After a period of time, the seal is removed from the gas ambient and the surface scanned with a radiation detector. Gas which has been entrapped in flaw locations can be detected in this manner.

Various dye tests[99,102] are employed for visual location of leaks. The seal is immersed in a penetrant liquid dye, sometimes under pressure. The dye penetrates fissures, cracks, or porosities and remains after surface cleaning. On standing, the dye seeps out of the flaws and becomes visible on the surface of the joint. Detection can be accomplished by visible color or fluorescence. The dye can also be applied to the inside of a seal and in time will penetrate through flaws and be detected on the outside of the seal. For very small leaks, the method requires a lengthy wait for the penetration of the dye. Gross leaks tend to flood the whole area of the seal and make flaw location difficult. The method lacks the sensitivity of mass spectrometer leak detection and does not provide a numerical measure of leak rate. Once used, the dye is very difficult to remove from capillaries and will continue to "bleed out." For the same reason, it is a source of contamination which makes the repair of a porous braze area difficult and unreliable.

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5.2.3 Thermal Tests

5.2.3.1 Thermal Conductivity

Thermal conductivity is the measure of the quantity of heat which will flow through the ceramic-metal joint of known area and thickness in a measured amount of time under the influence of a measured temperature differential between the faces. The characteristic is measured on a dimensioned joint by applying heat at one end and measuring the temperatures of the two parallel faces during a measured elapsed time.[103,104] The verification that thermal conductivity of the interfaces of beryllia-metal joints has a large effect on the heat dissipation properties of the whole assembly[104] has fostered interest in increasing the accuracy of this measurement and its application to the whole system, rather than to the individual components.

5.2.3.2 Thermal Shock and Cycling Resistance

The ability of an assembly to resist major, permanent damage when subjected to large temperature changes, whether sudden or cyclical is often important. Thermal shock resistance[27] of a joint is tested by heating the assembly to equilibrium at a predetermined high temperature and quickly immersing it into a fluid at a lower temperature. Cooling should be at a rapid rate and as uniform as possible over a complete assembly. The severity of thermal shock is a function of both the temperature differential and the cooling rate. Selection of the cooling fluid should be made on the basis of the cooling effect it exerts.

Thermal cycling[12] is performed by subjecting the joint to alternate pre-determined high and low temperatures with intervening time lapse schedules for heating and cooling. The test parameters for both thermal shock and thermal cycling can be varied over a wide range, depending on the use conditions to which the assembly will be exposed. Statistical data are obtained by examining and leak checking each assembly after each cycle and recording the number of defects.

5.2.4 Electrical Tests

5.2.4.1 Volume Resistivity

Characteristic of each material, volume resistivity is the resistance that a unit volume of the material offers to the passage of electrical current. It is measured as specified in ASTM D257-61.[105] Since volume resistivity changes with temperature, this and other environmental conditions of the part must be considered.

5.2.4.2 Breakdown Voltage

Voltage breakdown of an assembly or dielectric strength of a material is a measure of the potential difference which can be applied between two electrodes separated by an insulator before an avalanche

of current flows across or through the insulator.[106] The test is sensitive
to surface cleanliness of the ceramic. Conditions of the test, particularly
in reference to simulated atmospheres and altitudes, are detailed in
Government purchase specifications.

5.2.4.3 Dielectric Loss

Dielectric loss is the rate at which electrical
energy is changed to heat in a dielectric when it is subjected to an alter-
nating electric field.[107,108] The measurement of dielectric loss is a com-
plex procedure. In the Second Quarterly Report - Metallurgical Research and
Development for Ceramic Electron Devices,[107] by L. Reed, et al, an excellent
explanation of the nature of these losses and their measurement is given.

5.2.5 Specialized Tests

In addition to the foregoing routine tests which find appli-
cation both in the establishment of basic information and in day to-day con-
trol of quality, specialized tests are used. These tests are employed to
investigate phenomena and, once performed, are reused only occasionally to
verify the original finding or to investigate closely related phenomena.
Occasionally a phenomenon gains importance and intensive testing is undertaken
to gather data on its mechanisms and effects. In the case where the property
being tested is the result of a new product or has product potential, the new
testing procedures are adapted to quality control techniques and become
routine.

Tests of interaction or evaporation and condensation of joint
elements[109] during simulated use and electrolysis at seal areas under the
influence of direct current[110] can be cited as examples of specialized tests.
The resistance of joint components and interfaces to attack by a wide variety
of chemical elements and compounds over a wide range of temperatures[111,112,113]
is at present in the specialized test class. The increased use of such corro-
sive chemicals in battery applications,[73] thermionic energy converters,[12]
and nuclear applications[114] makes such tests candidates for standardization,
simplification, and routine use. Similarly, the advanced requirements for
aerospace applications of ceramic-to-metal joints are becoming standardized.[115]

New techniques arising from the introduction of new equipment
or the application of known techniques to new ends foster unique test pro-
cedures. The utilization of electron microprobe analyses[116] of joint areas
and of microhardness traverses of braze alloys in the joint[117] are contrib-
uting to the knowledge of better joint manufacture.

5.3 Failure Analysis

The employment of failure analysis is the most neglected area of
testing. Levinson,[118] noted that the importance of failure analysis cannot
be over-emphasized and his first recommendation stated a need for:

> "A program of exhaustive and definitive analysis of
> seal-insulator failures. Such a study would determine,
> by chemical and detailed metallurgical analysis, the

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failure mechanism. The utility of such information for intelligently coping with recurrent seal insulator failures and for anticipating future problems is obvious."

Visual examination, combined with intelligent analysis, plays the largest part in failure analysis of assemblies and can cover the range from macroscopic inspection to electron microscopy. This is obviously the first step of failure analysis. Color changes, especially discreet shadings, are noted and the extent and severity of gross failures and defects are observed. The effect of adjacent materials or interlayers on failure are subject to scrutiny and areas for closer, more detailed study are defined. Chemical, mechanical, and physical testing, used as supplements to visual examination, can often be used to verify these analyses.

Microscopic examination of polished sections of failure areas provide detail on which further analysis can be based. Pincus[119] detailed the application of taper sections (as proposed by Nelson)[120] to ceramic-to-metal seals and pointed out their usefulness in production trouble-shooting. La Forge[121] found that metallographic examination of polished sections of ceramic-to-metal joint areas provided control data and answers to failure problems where heat cycling, thermal shock, standard sealing tests, and low power surface examination had failed. Johnson, et al[94] performed a leak path study by allowing a penetrant dye to enter the leak path, converting the dye to a black carbon track and tracing the track by high power metallographic examination of sections of the joint to identify the flaw.

Failure analysis is not complete, no matter how conclusive an obvious explanation seems to be, until the correction of the failure is effected by a change in design, material, or processing which is suggested by the analysis. If the change does not produce relief from failures, an indication that the failure analysis was incorrect or incomplete can be surmised.

5.4 Testing State-of-the-Art

The state-of-the-art of testing ceramic-to-metal joints is typified by a multiplicity of tests and test procedures, carelessness in recording and reporting test conditions, materials tested and even test results, by exaggeration of test values, by faulty interpretations and by empiricism. The reasons that these conditions exist are complex. The large number of test methods is, in part, symptomatic of an advancing technology and reflects a dissatisfaction with the status quo and a search for better, more reliable, and more reproducible methods.

The newness of ceramic-to-metal joining as an industry and the nature of ceramic materials add to the difficulties in obtaining reliable and reproducible test results The variations in ceramic components, whether between various manufacturers' products or in lot-to-lot inconsistencies, often obviate reproducibility. Attempts have been made to apply testing procedures which have been established to determine the strength of metals and metal-to-metal joints. The wide disparity in mechanical strength properties of metals and ceramics should make it apparent that direct applications of such test

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methods will not produce direct comparisons of strengths. Shook[62] in reporting on test methods for brittle materials found that a supplier very often reported test results in the form of a single number with little or no accompanying information on the conditions of the test, the specimen size, the equipment used or the other conditions which would be pertinent to, and in fact necessary for, a reasonable evaluation of the data. King[27] tested ceramics as received and found that strength values varied considerably from the figures given by the manufacturers. Property data supplied by a fabricator, whether of the ceramic body or the ceramic-to-metal joint, is most often included in a sales brochure. As such it is considered sales data rather than property data. Overstatement of the data by publication of the maximum is practice. The fact that these data are frequently used for design purposes places a burden on the honest reporting of facts.

The Alumina Ceramic Manufacturers Association has made an attempt to standardize test methods and to specify acceptable values for many of the properties of high alumina bodies.[102] Twenty-one electrical, physical, mechanical, and thermal properties are listed with reference to test methods and principal testing conditions. Alumina bodies are divided into three classes according to per cent alumina: 80-90, 90-96, and over 96. A generous and often overlapping range of values for each property is given for the three groups. Test methods range from the precise evaluation of thermal expansion coefficient by interferometer or dilatometer to the following statement on working temperature:

> "Working temperature is the maximum safe temperature for
> continuous use when the parts are completely supported.
> The manufacturer's experience with conditions of appli-
> cation of the ceramic part will be the governing factor."

A committee of the American Society for Testing and Materials is presently at work with the purpose of establishing a specification for alumina ceramics. While the purpose and accomplishments of the ASTM are admirable, certain weaknesses in its specifications exist:

1) The final document represents the opinions of a committee and the final specification can only be a compromise of the judgment of users and suppliers. As a result, test methods are detailed with too wide a latitude of equipment and procedures for a reliable comparison of data between different investigators.

2) The establishment of such a specification, which is the result of more-or-less spare time effort on the part of the committee members, requires a long-term effort, often measured in years.

3) Once established, such a specification is very difficult to modify in spite of weaknesses which become apparent in initial usage and application.

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The importance of good test methods in any process is elementary. The benefits that can be derived from precise, reproducible, and accurate test methods could form a lengthy dissertation. Of primary importance is the increase in applications of materials or products whose properties and potentialities are most precisely and accurately known.

The establishment of uniform testing procedures which can be uniformly applied with high reproducibility will do much to simplify customer-producer efforts to arrive at the design which will be a balance between reliability and cost. Purchasing specifications, whether Government or civilian, will be simplified and product confidence will increase. A lowering of assembly cost could logically be expected to result because the lengthy procedure of prototype testing, modification and redesign, and retesting would be considerably shortened in many cases.

The need exists for a dual standard system of testing for ceramic-to-metal joints. The investigation of true property values will require a precise, accurate, reproducible set of testing methods. All ambient conditions of such tests must be controlled to the greatest degree possible, and any conditions which cannot be controlled precisely must be notated with all information that is available. The aim of such tests will be toward the attainment of absolute values. For comparison testing, on the other hand, a second set of standards will be required for which accuracy will be secondary to reproducibility The aim of this second group of tests will be to obtain sets of values to which a constant factor can be applied to produce relatively true values. Ideally, the comparison tests should be simple, inexpensive, and require little expenditure of time with semi-skilled labor. Ambient conditions, within reasonable limits, should not affect test results but it would be desirable to note the conditions of the test on data sheets. For comparison testing, a low cost standard sample should be available for initial establishment of the effect of process parameters on the factor to be applied to attain a true value. Such a sample would also be useful in periodic checks on the test method.

An established system less than ideal which would produce some measure of standardization would be preferable to the confusion that exists in the present system of a multitude of test methods with little common ground for comparison of results. A common test method, weak as it may be in the beginning, could be expected to create and foster a unified effort for improvement. This effort would encourage more sharing of detailed information. An improvement in testing in a common system would be of little value for comparison if only one person used the improved method.

The speed with which ceramic-to-metal joining technology advances toward becoming a science will be dependent largely on the speed with which reliable basic knowledge of materials and products is accumulated. Reliable, reproducible testing methods which generate useful data will, at the same time, increase the degree of confidence which the potential user has in the products.

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6. Theory of Ceramic-to-Metal Joining

6.1 General Consideration

To date, no major insoluble problems have been encountered in the field of ceramic-to-metal joining. However, because of the lack of formalized understanding of the underlying physical and chemical principles of ceramic-metal bond formation, the technology has developed on a very empirical basis. The formulation of an entirely acceptable bond theory has been hindred by the large number of variables associated with the preparation of good joints. An adequate knowl dge of the bonding mechanism would likely lead to considerable improvement of existing joining techniques, and to the evolution of better combinations and techniques.

It is the purpose of this section of the report to discuss the present concepts of ceramic-metal bonding theory, to elucidate the complexities involved in the experimental disclosure of the fundamental bonding mechanisms, and suggest the direction of additional experimental work. The primary source of information for the theoretical aspects of ceramic-to-metal joining has come from workers in that field of endeavor. However, other interesting and often ignored information has been taken from studies and explanations of bonding such as in glass-to-metal seals, cermets, adhesives, thin films, friction, and basic theories of interatomic bonding and structure.

Bonding of ceramics to metals is considered to be the result of chemical and/or mechanical interactions between the materials. The chemical interactions may either result in the formation of new compounds or in weaker attachments through attraction due to secondary bonding forces. The mechanical interactions are the result of the interlocking of one phase with the surface roughness of the other as in Fig. 2. The roughness may be derived from mechanical deformation of the structure or from localized chemical attack. There must, of course, be sufficient mobility of one phase on the other to allow the interpenetration with the surface irregularities needed for interlocking.

A ceramic-to-metal joint is generally made at some high temperature. Its so-called strength is usually measured at a much lower temperature by an arbitrarily chosen technique. A typical measured strength is less than 10,000 psi.[51] In any discussion of the theoretical aspects of ceramic-to-metal joining, the relationship between this measured strength and the theoretically attainable strength should be defined. The factors which together produce the observed or measured strengths of ceramic-to-metal bonding are represented schematically in Fig. 3. For convenience in the present discussion, the information of Fig. 3 can be expressed in an
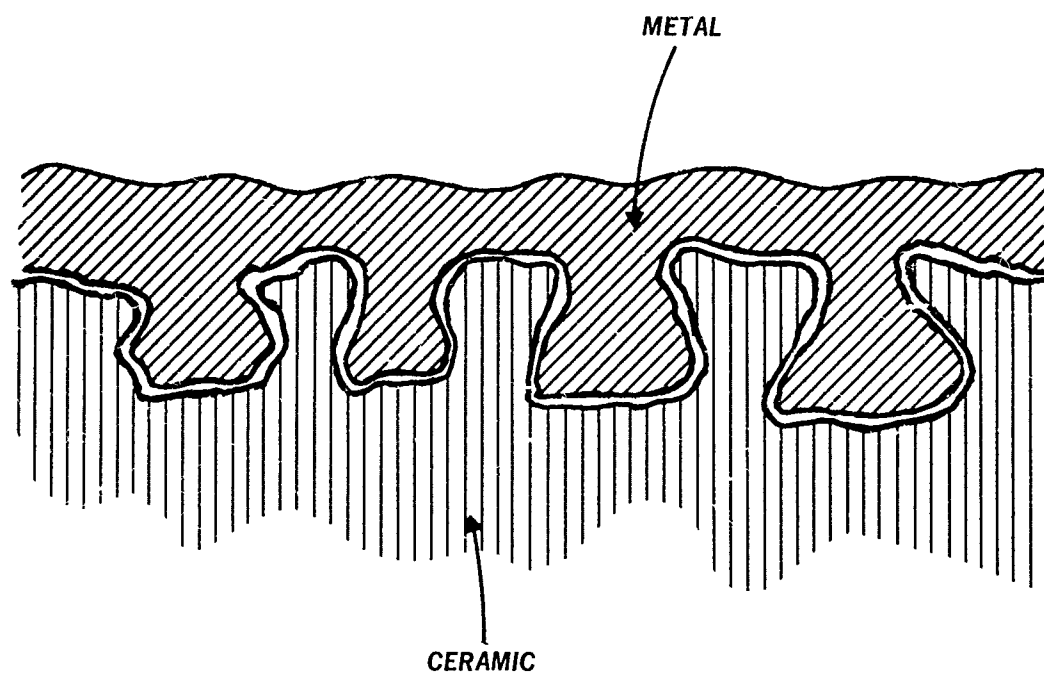
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Figure 2 . — Mechanical interlocking of metal and ceramic structures.
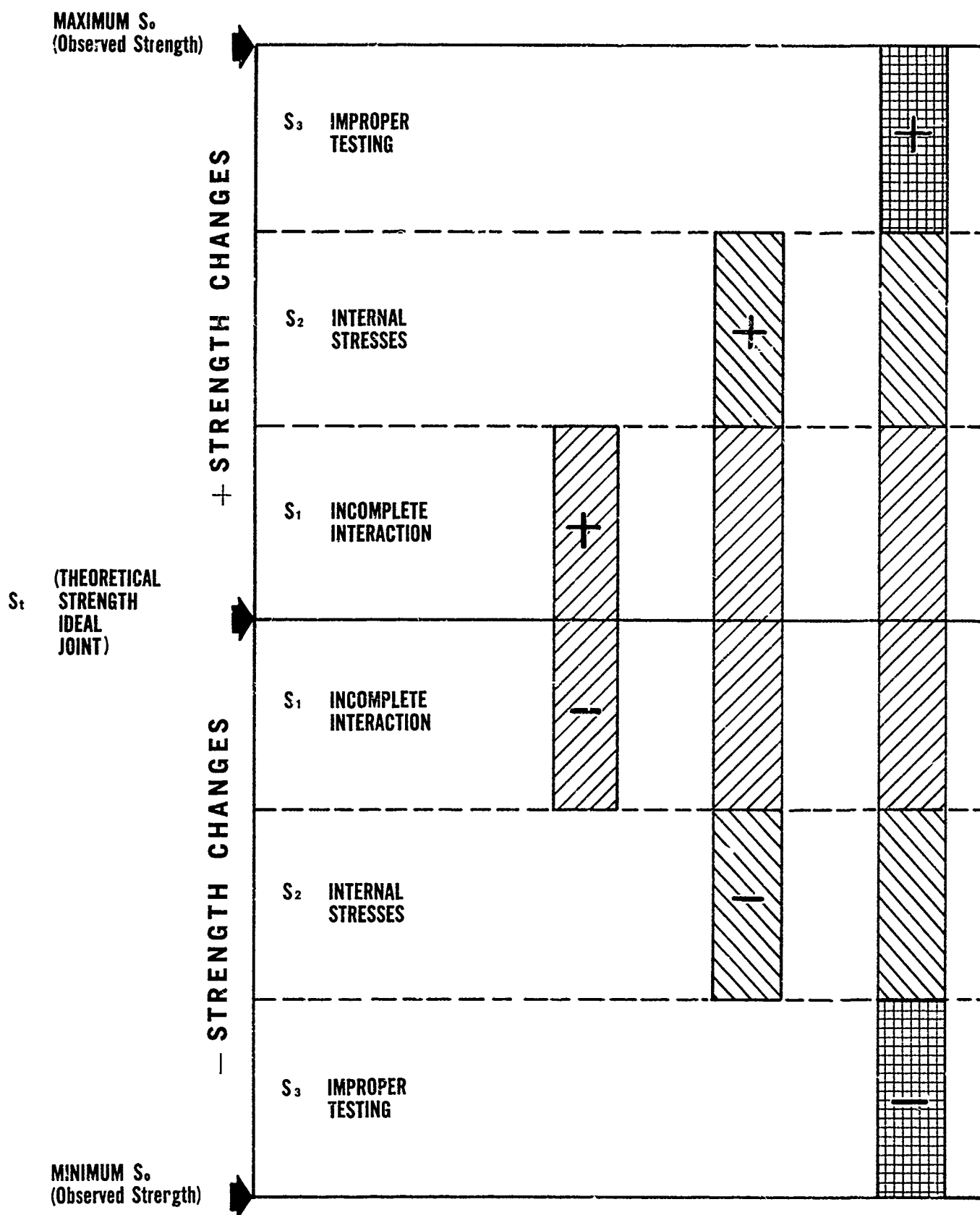
Figure 3. — Bar graph representation of the limits of observed ceramic-metal joint strength which may occur because of strength changes resulting from incomplete interactions, internal stresses, and improper testing.

equation:

$$S_o = S_t + S_1 + S_2 + S_3 \qquad\qquad (1)$$

where:

S_o is the observed strength of a real joint
S_t is the theoretical strength of an ideal joint
S_1 is the strength change due to incomplete interaction
S_2 is the strength change due to internal stresses
S_3 is the strength change due to improper testing

Although ceramic-to-metal joining theory is discussed in this report with specific reference to strength, it must be remembered that a similar analysis of the bonding can be made using other parameters, such as thermal conductivity or vacuum tightness.

6.1.1 Theoretical Bond Strength

The theoretical strength of a ceramic-to-metal joint, S_t in equation (1), is determined by the nature and magnitude of chemical bonds which must be broken in the acting failure mechanism. This is true whether the bonding in the joint is chemical or mechanical, since, in either case chemical bonds must be broken to destroy the joint. These chemical bonds are derived from various sources of attractive forces among atoms or molecules and may be divided into primary bonds and secondary bonds (in this report chemical bonding forces shall include the secondary attractive forces often termed physical forces[122] depending on the relative strengths attainable from each. Primary bonding forces are those responsible for formation of compounds and radicals and there are three classifications - metallic ionic, and covalent. The weaker secondary bonding or van der Waals forces are classified under orientation, induction and dispersion bonds.

6.1.1.1 Primary Bonds

There is a tendency of all atoms to attain the electron configurations of the inert gas structures, i.e., filled outer electron shells. This may be done by either adding electrons to the outer electron shell already present or by removing all of the electrons from it, such that the filled shell just inside of it will become the outer shell. A transfer of electrons from one type of atom to another in order that both may attain filled outer shells produces opposite charges in the atoms resulting in attraction and bonding. It is this bonding that is termed ionic. Ionic bonds and to a lesser extent the covalent bonds are considered to be the main bonding forces in ceramic materials. Aluminum oxide is a typical ceramic containing ionic bonding.

The formation of the covalent type of bond is the result of a sharing of electrons among adjacent atoms to obtain the outer shell configuration of an inert gas. This bonding is not only thought to hold the atoms of soft low melting organics together, but also such hard high melting point crystalline substances as diamond and silicon carbide.

Metallic bonds may be pictured as resulting from attraction between metallic cations and free electrons moving in their interstices in a continuous set of energy levels. It is this continuous set of free electrons that is responsible for electrical conductivity in metals. Some uncertainty, as to the exact nature of these bonding forces, still remains. For instance, Pauling,[123] has pictured the metallic bonds as resonating covalent bonds. This is in variance to the first description given above, which was based on development of Drude's original free-electron-gas theory.[124]

Theoretical calculations based on perfect lattices indicate that materials with primary bonding should have strengths (10^6 to 10^7 psi) over an order of magnitude greater than the strengths normally observed. The low strengths have been shown to be due to lattice imperfections and, in the nearly perfect structures found in whiskers, strengths approaching theoretical have been observed.

6.1.1.2 Secondary Bonds

These forces are usually considered to be quite weak. However, if the assumptions upon which Humenik and Whalen[125] based their calculations are accepted, the energies of secondary bonds may often be sufficient to produce strengths (10^5 to 10^6 psi) greater than normally encountered with primary bond forces in ceramic or metallic bodies. These secondary bonding forces, often termed van der Waals forces, result from asymmetry of the charges in atoms and molecules and the greater the asymmetry the greater the force.

Glasstone,[126] has discussed the orientation, induction, and dispersion effects which are responsible for secondary bonding. The first explanation of secondary attraction, based on the orientation effect, was presented by W. H. Keesom in 1912 and 1922. He attempted to explain molecular attraction as due to the interaction of permanent dipoles in the molecule. The magnitude and size of the force (which could be either attractive or repulsive) depends upon the orientation of dipoles such as would be expected with polar molecules like those of water. If all orientations were equally possible, the resulting energy would be zero. However, statistical considerations indicate a preference to certain orientations. If this orientation effect produced the only acting force of molecular attraction, it would be expected that the bond strength would be reduced rapidly with increasing temperature. This is not entirely in accordance with facts, and P. Debye in 1920 and 1921 suggested that the moment induced by dipolar molecules on adjacent molecules could cause an additional attractive force, the induction effect, which is independent of temperature.

Glasstone has pointed out, however, that two difficulties may be encountered in the effects described above: (1) although the interaction energies are applicable to a pair of molecules they are not additive for all the molecules in a gas or liquid - in fact, since many different molecular arrangements are possible there may be significant cancellation of energies, and there will be no attractive force to account for cohesion; (2) many molecules which do not have permanent dipoles exert appreciable attractions on one another. London in 1930, using the principles of

quantum mechanics, showed that all molecules must possess energy, even in their lowest states. Consequently, even with monatomic molecules, the nuclei and electrons must be regarded as having some vibration with respect to each other, forming temporary dipoles. For molecules with no permanent moments, the average of these configurations produce a zero resultant. The temporary dipoles, however, may induce dipoles in other molecules causing attractive forces. These forces are said to be due to the dispersion effect, because the oscillations which produce the dipoles are also responsible for dispersion of light by molecules.

The bonding strengths due to these effects are considered to decrease in the order: orientation forces, dispersion forces, and induction forces.[127] The energies of all three are shown to vary as the inverse ratio of the sixth power of the distances between the molecules, and therefore very close contact between phases is absolutely necessary to the formation of a strong secondary type bond.[128] Under certain conditions, therefore, any of the types of primary bonds in the presence of secondary bonds may be represented in a ceramic-to-metal joint or a gradation of primary to secondary bonds may exist.

6.1.2 Incomplete Interactions

The interphase contact necessary to the formation of ceramic-metal bonding may be attained through solid state interactions or, more rapidly, through the use of transient liquid or gaseous phases. Often, complete contact between the ceramic and metal is inhibited through inhomogenities at the surfaces of both materials. A qualitative picture of these surface features may be obtained by considering some of the aspects of the formation and structure (macroscopic and microscopic) of the materials.

The ideal solid consisting of a perfect single crystal with atomically smooth surfaces is non-existent. The most perfect crystals found in nature or produced in the laboratory contain surface variations of at least tens of angstroms, and usually several orders of magnitude greater. The variations may be the result of growth spirals, particles entrapped in growth, adsorbed films or particles, unattached substances on the surface, localized chemical attack, or mechanical deformation. Further, the occurrence of massive single crystals is quite infrequent, as nucleation phenomena usually result in the formation of polycrystalline substances. The crystals which make up materials will ordinarily exist together in a variety of orientations joined at grain boundaries, where directional forces associated with the orientation of each grain are in competition. When sufficient activation energy is provided a balancing of these forces takes place producing surface distortions - as in thermal etching. In addition, during the formation of the joint additional impurity phases may be ejected from the bulk phases and become entrapped at the interface.

The various surface irregularities which prevent total ceramic-metal interaction may decrease the ceramic-to-metal bond strength through the formation of stress raisers or notches, formation of fewer or weaker chemical bonds, or through the reduction of any mechanical interlocking. Or, in contrast, strengthening may result through increased mechanical bonding to the

irregularities or from the formation of stronger chemical bonds through an impurity phase bonded to both the ceramic and metal. Therefore, S_1 of equation (1) may be positive or negative.

6.1.3 Internal Stresses

The internal stress at the interface between a ceramic and a metal, S_2 in equation (1), may be mechanically, thermally, or crystallographically induced. Mechanical strain might be present as a result of plastic or elastic deformation; thermal strain could be caused by the stress set-up in cooling joined materials with different thermal expansions or through cooling portions of the joint at vastly different rates; and crystallographic strains may result from lattice mismatch[129,130] and phase changes. However, the stress is usually[43,131,132] attributed to just one of these sources - the stresses set up by cooling joined materials with different thermal expansions. Bondley[132] showed that a strength change for that case could be determined from the relation:

$$S_E = (T_1 - T_2) \ (K_m - K_c) \ \frac{E_m E_c}{E_m} + E_c \tag{2}$$

where S_E is the stress resulting from the expansion differences, T_1 and T_2 are the temperatures of joint formation and strength measurements, K_m and K_c are the temperature coefficients of expansion for the metal and ceramic, and E_m and E_c are the respective moduli of elasticity of the metal and ceramic. For typical materials and joining temperatures, S_E can have negative values in excess of 50,000 psi.

The internal stresses at the interface may add to or subtract from the stresses caused by applied loads, and may therefore either strengthen or weaken the materials. Depending upon distribution and magnitude of the stresses, then, S_2 may be positive or negative.

6.1.4 Testing

As has been pointed out, current test procedures do not provide an adequate measure of joint strength. The actual distribution of stresses in the materials and at the bond interface are seldom, if ever, known. In addition, it may not be possible to even adequately duplicate conditions from one test sample to another. Tests are designed to provide data on the action of a particular stress vector or vectors on a ceramic-to-metal joint. However, the applied stresses may be resolved into various components and test measurements may give results either lower than or in excess of the stress or stresses which the test was designed to represent. Hence, S_3 in equation (1), can also be positive or negative.

6.2 Ceramic-Metal Bonding Theories

The information for theories of bonding between ceramics and metals have developed primarily from two different classes of experiments. The first class is based on preparation and investigation of ceramic-to-metal, and as a result has received the greatest attention from those involved in manufacturing ceramic-to-metal seals. The second class is based on studies of wetting and interfacial reactions between solid and liquid ceramics, glasses, salts, and metals.

6.2.1 Theories Developed from Studies of Bonding in Ceramic-to-Metal Seals

The U.S. patent issued to Pulfrich in 1939[1] for a ceramic-to-metal joining technique, which has been previously referred to, has served as a basis for the development of many of the processes in current use. In it, refractory metal powder was first sintered to the surface of a ceramic and then joined to another piece of metal by soldering or brazing. The composition of the steatite body used in his work was considered quite important, and he specified that it have a large vitrification range with the fusion point of a eutectic or low melting point solid solution at its grain boundaries being several hundred degrees centigrade lower than the softening point of the ceramic body as a whole. Also, the melting point of the ceramic and the metal powder had to lie considerably above the temperature at which the powder was to be sintered to the ceramic body. According to his observations, the metal powder is entrapped by the molten portions of the ceramic surface and becomes undetachably anchored after cooling at which time the entire body consists of a uniform crystal structure free from vitreous portions.

Nolte and Spurck in 1950[4] ascribed the active metal bonding of titanium, zirconium, and their alloys to ceramics, for use in the preparation of seals, to chemical reaction; but did not attempt a more detailed explanation. They did, however, give an interesting discussion of the bonding developed in the application of their modified version of Pulfrich's refractory metal powder technique. For this technique the refractory metal powder was molybdenum and it was found that an addition of manganese powder insured reproducible good bonding to all ceramics without the aid of finely divided metal powders and special protective atmospheres. On the basis of their work, it was proposed that to bond metallizing powder to ceramic, it is necessary to chemically combine them through the formation of eutectics or solid solutions of the metals and ceramics. The role of manganese in the metallizing was thought to be that of a stimulant, reacting with the ceramic to provide a means whereby the molybdenum might combine with the ceramic. No evidence of any chemical reactions was offered. It was also suggested that the molybdenum powder was important as a source of pores for mechanical interlocking.

Pincus in 1953 and 1954[30,119] reported on seals made using molybdenum metallizing both with and without addition of manganese. For the studies of the molybdenum-manganese process, high alumina (96% Al_2O_3) and fosterite bodies were used. He pointed out that even if the hydrogen used for this type of metallizing has a very low dew point, say -65°F, the

manganese will be totally oxidized in the course of firing. The MnO produced is said to form resinous looking lumps at 1000°C which attract particles of the molybdenum powder. The MnO then alters to a grayish slag and as the temperature is increased liquid is formed at the ceramic-metal interface. This liquid moves into the metal layer and also corrodes the ceramic surface, while the MnO slag moves to the ceramic-metal interface. With continued heating, at the normal firing temperature of 1400°C, more and more alumina dissolves in the slag followed by the crystallization of galaxite and then corundum with progressive weakening of the seal. The best bonding results are obtained with the most extensive development of glassy phase.

Although it could not be observed, it was hypothesized that for molybdenum and manganese on fosterite the MnO slag described above again forms and interacts with the ceramic. However, in this case, the structure formed on cooling contains no glassy phase since the MnO crystallizes into the fosterite structure. The molybdenum is described as being locked into the fosterite - intimating at least some mechanical bonding. For studies of the effect of molybdenum alone, Pincus metallized high alumina ceramics with molybdenum and molybdenum oxide powders in hydrogen atmospheres with controlled dew points. Binding strength measurements were made on joints prepared from the metallized ceramics. On the basis of the results observed, he found the following features to be associated with the formation of a good bond: (1) the metal (molybdenum) must be oxidized a controlled amount, (2) chemical reaction between the metal oxide and the ceramic must form an interface zone, and (3) bonding between metal and ceramic through the interface must produce a graded, continuously coherent structure. Oxygen for the oxidation of molybdenum metal in hydrogen at high temperature was believed to have come from dissociation of impurity oxides in the ceramic - principally silica. Pincus' ideas received particularly wide attention, and his observations form the basis for what has been termed the "alumina reaction theory of adherence."[133]

La Forge in 1956[134] suggested that for preparation of a good joint with the molybdenum-manganese process, it is necessary for fluxes in the ceramic to become sufficiently fluid at the metallizing temperature and available for reaction. It is also considered important that the joining temperature be high enough to cause the metal particles to sinter together in a strong coherent mass. Excessive migration of the fluxes into the metal powder was reported to reduce strength by coating the powder to such an extent that strong solder or braze bonding to the metallizing is not possible. It was proposed that activating metals, such as manganese, may be unnecessary when flux concentrations are high.

Denton and Rawson in 1960[31] reported on the roles of MoO_3 and Mo-Mn compositions in forming bonds. They showed that aluminum oxide greatly retards the evaporation of MoO_3 on heating and indicated that it is the result of compound formation between molybdenum oxide and alumina. It was suggested that of the fluxing oxides commonly found in high alumina ceramics, i.e., SiO_2, CaO, and MgO, molybdenum oxide would be likely to react only with MgO or CaO since SiO_2 is acidic. In the molybdenum manganese process the explanations of Pincus are generally supported. It was also

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pointed out, however, that reactions with flux oxides could be of importance. They found fine grain size ceramics easier to metallize.

The explanations of Cole and Sommer in 1961[135] were based on experiments with 100% Mo, 80% Mo-20% Mn, and 97% Mo-3% Ti, metallizing mixtures. The metallizing was done in a hydrogen atmosphere on a high alumina ceramic containing a glassy phase (the flux constituents used to aid in densification of the ceramic body) and on one in which there was almost no glass phase. From the results obtained in these experiments, they proposed that the primary source of bonding is migration of glassy phase into the pores of the sintered metal powder. Oxides formed of minor metallizing constituents, like the Ti and Mn above, enter into solid solution with the glassy phase of the ceramic and either promote wetting or increase glass strength, thereby strengthening the bonding. Where little glass phase is present in the ceramic for such bonding, they have suggested that weaker bonding may be due almost entirely to reactions of the minor metallizing constituents to form compounds capable of wetting both ceramic and metal particles; or this bonding may be due to ionic exchange of a solid state nature resulting in adherence in the first few molecular layers. These explanations have received as wide attention as those proposed by Pincus and have been termed "the glass migration theory of adherence."[133]

In 1962, Floyd[51] presented a mechanism for the adherence between high-alumina ceramics containing glass phase and molybdenum-manganese metallizing. Flux composition was given close attention, and bodies containing three variations of SiO_2-MgO-CaO glassy flux as impurity were used in preparation of joints. He found increased strength to be associated with increasing concentration of glassy phase and with the formation of manganese spinel in the metal powder layer. From this he concluded that the features of the "alumina reaction theory" of Pincus and those of Cole and Sommer's "glass migration theory," are both necessary to the production of strong bonds. In contrast to the work of Denton and Rawson, he found that increasing crystal size in the ceramic results in increasing strength.

In 1964, Helgesson[136] reported on the bonding in seals prepared from molybdenum-manganese mixtures on high alumina bodies. His work indicated that higher alumina ceramics give greater seal strengths - in particular, silica additions to the metallizing cause a decrease in strength. He concluded that chemical bonding between the ceramic and metal is responsible for bonding with this type of metallizing.

Cowan, Herrick, and Stoddard in 1964[137] presented the results of an investigation to devise a technique for the preparation of ceramic-to-metal seals to be used in thermionic converters. Seals were desired which could withstand attack by cesium at 1500°C. Seals containing silica, titania, or manganese oxide could not be used because of cesium attack, thus precluding the use of the more common ceramic-to-metal joining processes. Very promising seals were made with silica-free high alumina bodies. Good metallizing was obtained in a hydrogen atmosphere (dew point, -25°C) with tungsten powders when small additions of yttria were added to either the tungsten or to the alumina body used. The following sequence of reactions was proposed to be responsible for the adherence of tungsten to a silica-free body containing a small addition of yttria:

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(1) Some WO_2 forms at low temperatures and may be retained, in part, to about 800°C.

(2) The WO_3 reacts with yttria or yttrogarnet in the grain boundaries of the ceramic.

(3) As the firing temperature is increased, unstable yttrium tungstates are reduced to yttria and tungsten, and migration of yttrium (as yttria and yttrium tungstate) proceeds into the tungsten powder.

(4) At the final firing temperature of 1700°C the tungsten densifies and the mixture of tungsten, yttrium tungstate, and yttria coalesce into a hard, dense structure.

In 1964, Kiwak[19] discussed several modifications of the tungsten-yttria metallizing, and indicated that better seals for thermionic converter use could be obtained with a $Mo-Y_2O_3-Al_2O_3$ cermet metallizing. On the basis of his observations he proposed that bonding of this mixture to high alumina ceramics was the result of the formation of an alumina-yttria eutectic which produces a ceramic braze for joining the ceramic and metal powder.

6.2.2 Studies of Wetting and Interfacial Reactions

When a droplet of liquid is placed on a solid surface it may spread to increase interfacial contact or remain in an essentially spherical form so the number of unattached bonds at the surface may be kept to a minimum. The thermodynamic driving force for any spreading (often called wetting) that occurs in such a system is a decrease in its free energy. When the solid surface involved is perfectly flat and clean and the temperature is such as to allow residual stresses to be relieved, the surface energies (analogous with surface tension for these conditions) may be related according to the Young-Dupre equation:[138]

$$F_{sv} - F_{sl} = F_{lv} \cos \theta \qquad (3)$$

where F_{sv}, F_{sl}, and F_{lv} are respectively the solid-vapor, solid-liquid and liquid-vapor interfacial free energies, and θ is the contact angle or wetting angle (see Fig. 4). Theoretically, the bond energy of the solid-liquid interface may be expressed in terms of the surface energies, neglecting the presence of any interfacial stresses. This bond energy is represented by the work required to pull apart a unit area of interface at a given temperature, creating an additional unit area of surface on the droplet and on the solid. This may be represented by the relation[125]

$$W_A = F_{sv} + F_{lv} - F_{sl} \qquad (4)$$

where W_A is the bonding energy or work of adhesion. In light of equation (3) above, equation (4) may be modified to the form
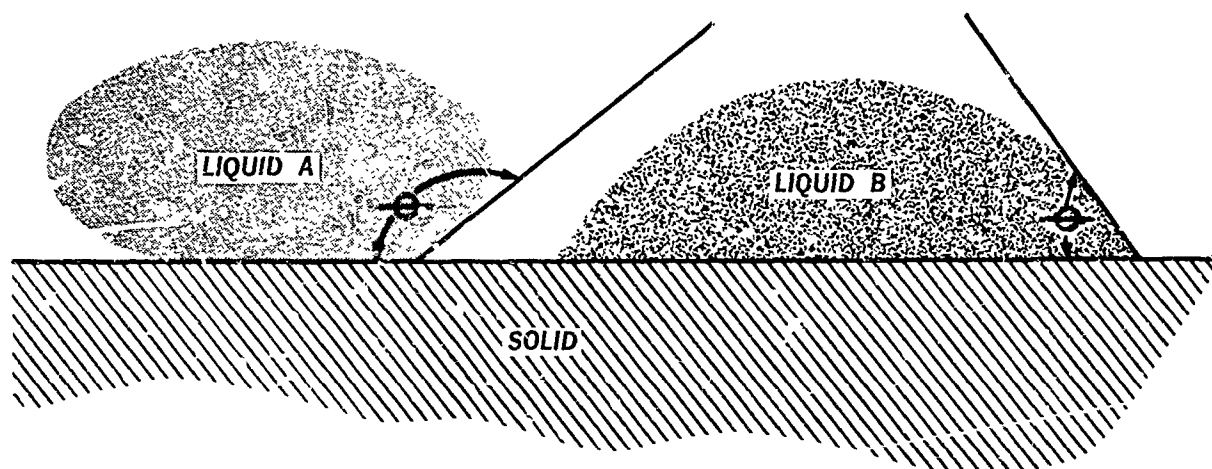
$$W_A = F_{lv} (1 + \cos \theta) \qquad (5)$$

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Figure 4 .— Typical contact angles of liquid droplets on a solid.

If, as Bondi[139] has assumed, most of the energy required to separate the droplet from the solid is expended in about the first angstrom of separation, then, even at high wetting angles, the interfacial strengths may be greater than the actual strengths of the components. However, it must be remembered that nucleation and fracture mechanisms may act to substantially reduce the strength at the interface.

Many workers in the field of joining have taken the thermo- dynamic approach based on the ideas of wetting and adhesion. Measurements of interfacial energies and contact angle have been used to indicate the bond strength. It should be noted, however, that portions of the usual thermo- dynamic interpretations of wetting and adhesion have been subjected to con- siderable criticism.[140] Since by its very nature, thermodynamics ignores details, it cannot be used to describe the atom-atom interactions responsible for adhesion.

The need for a complete atomistic picture from which descrip- tions of the interactions necessary for good bonding (in any system) could be obtained has led those investigating wetting and adhesion to closely examine the ceramic-metal interfacial region for chemical reactions and changes in lattice structure which could be associated with wetting and adhesion. Even where no reaction products have been directly observed they have been postu- lated on the basis of the compositions of the materials placed in contact through the interface. Investigators such as Kingery, et al[141-147] Armstrong, et al[148-150] and Sutton[88] have examined metal-ceramic reactions and the effects of certain elements which have been found to aid in the forma- tion of ceramic-metal bonds, e.g., O_2 and Ti, but did not develop a microscopic theory of the joining mechanism.

According to Humenik and Whalen[125] in a discussion of bond- ing in cermets, the generally accepted requirement for the formation of a strong bond between the metal binder and the nonmetallic phase is mutual or partial solubility. They have also pointed out, however, that the formation of an oxide of the metal at the interface would lead to better bonding. Van Vlack[151] extended the first requirement given above to also cover the enhancement of bonding through the presence of oxide of the metal component at the ceramic-metal interface. He suggested that good bonding may occur when the reaction provides a boundary which grades from the metal phase to the ceramic phase-accomplished through solution in the solid metal phase (e.g., oxygen in titanium) or solution of metal ions in the ceramic.

Several interesting joining theories, which are at least qualitatively atomistic in nature, have evolved in the course of studies of glass- and salt-metal wetting and adhesion. The bonding in such systems must be similar to that in ceramic-metal systems, since the bonds in ceramics are the same as those in glasses and salts. The theories of Weyl, et al[152,153] King, et al[154] and Pask[155] in this area are regarded to be sufficiently pertinent to ceramic-metal bond theory and well-backed with reason and experi- mental evidence to justify their inclusion in this report.

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On the basis of experimental investigation, Weyl, et al, (152,153) have developed an explanation or theory for the adhesion of certain glasses and fused salts to metals. Their studies were not of "wetting" in the strict sense of the word, as no contact angles were measured. However, it was assumed that without low liquid-solid contact angles adherence would be poor and wetting was therefore used to indicate the likelihood of adherence. Two sources of adhesion of glasses and salts to metals were proposed:

(1) Continuation of the structure of the glass or salt through oxides on the metal surface.

(2) Attraction (secondary bonding) resulting from the forces at the glass or salt surface inducing a reflected electron distribution pattern in the metal - the stronger the forces the stronger the adhesion.

The factors affecting the second source of adhesion were closely examined in their studies, and it was concluded that the adhesive strength or lack of it may be derived from the ability of polarizable ions in the surface of the particular glass or salt to deform and reduce the emanating surface forces. An inability to deform would be reflected in stronger adhesion. It was also pointed out that the surface forces might in some cases be reduced to such an extent on crystallization of the liquids, that adherence would be lost.

King, Tripp, and Duckworth(154) conducted experiments to determine the source of adhesion in enamel (glass)-metal systems. They considered wetting, or rather good spreading, of the molten enamel on the metal to be necessary to the development of a good bond. No contact angles were measured as the authors were only concerned with how well the glass spread out and covered the surface - very low contact angles were required. Their theory as illustrated in Fig. 5, contained three major conjectures:

(1) For bonding to occur, the enamel at the interface must be saturated with an oxide of the metal which, in solution in the glass, will not be reduced by the metal.

(2) Saturation of the glass interface with the metal oxide causes metal ions to be forced into surface positions.

(3) The metal ions in the glass are joined to the atoms in the metal surface and form a bond that is a transition between that in the metal and that in the glass.

Pask,(155) on the basis of his investigations of glass-metal wetting and adherence, has developed the most recent theory of glass-to-metal bonding. It was his supposition that the fundamental requirement for good adherence of glass to metal is the formation of strong chemical bonding at the interface. The bond was described as being the result of transference or sharing of electrons at the junction of the two phases (glass and metal) in

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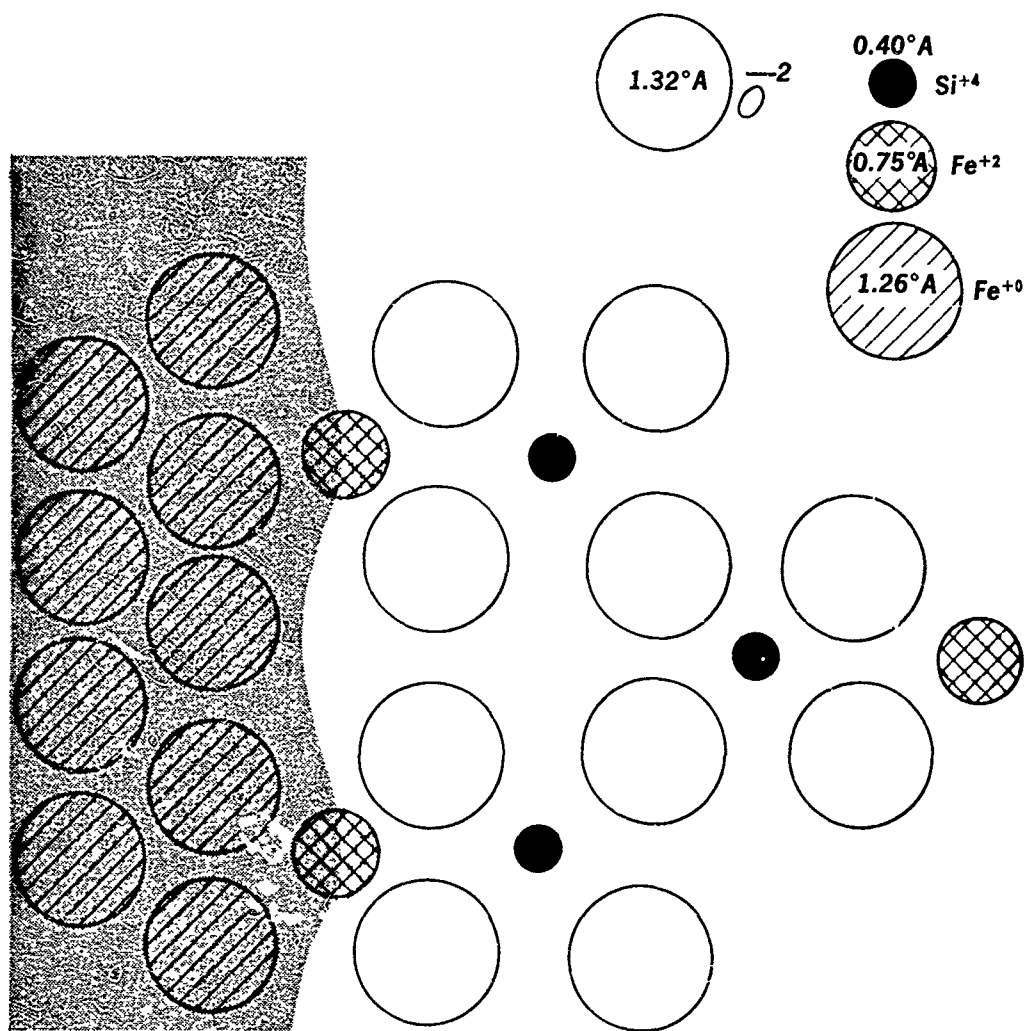
Electron cloud

Figure 5 .— Schematic representation of bonding through a glass-iron inter-face. (154)

equilibrium. He gave three chemical factors important to the balance of bond energies necessary for good bonding:

(1) The two phases in contact must be in thermodynamic equilibrium (permissible latitude is unknown).

(2) The glass and metal are not in thermodynamic equilibrium in an open system.

(3) An intermediate " -ous oxide layer" is needed. (The layer, under these conditions, can be monomolecular.)

    (a) The metal must be in thermodynamic equilibrium with this oxide.

    (b) The glass must be in thermodynamic equilibrium with this oxide. (The glass at the interface must be saturated with this oxide.)

Figs. 6 and 7 schematically represent his picture of the conditions under which van der Waal's bonding (which he considers to be very weak) and chemical bonding (strong bonding) occur. He has stated that if the glass crystallizes (producing a ceramic-to-metal seal), bonding will be made more complex due to the additional problem of epitaxial fit.

6.3 Criticisms of Bonding Theories

When the above theories are critically examined in the light of equation (1), it is evident that the main emphasis has been only on certain limited aspects of S_t, the maximum theoretical strength; and on negative values of S_1, the strength lost by incomplete interaction. While some offer feasible explanations of the adherence of a metal to a ceramic, no correlation between S_o, the observed strength and S_t, the theoretically attainable strength of the joint, can be made. The so-called theories of ceramic-to-metal bonding which have been reviewed are obviously little more than descriptions of the observed and postulated interaction phenomena which have been associated with the formation of good joints. It has not been experimentally established what part, if any, the phenomena may play in the formation of bonds. It is not unlikely that many of them appear simply because they occur under conditions similar to those required for good bonding.

While the theories postulated for glass-metal bonding are more definitive, they are based on rather indirect experimental evidence and are too qualitative in nature to allow theoretical bond strengths to be calculated for comparison with experimental values. In addition, it may be difficult to apply glass-metal bond theory to the formulation of ceramic-metal bond theory as it does not take into account the relatively fixed positions required of the atoms in a crystalline lattice.

Many of the investigations of ceramic-to-metal bonding have been excellent pieces of work. However, it appears that it was not initially recognized just how many variables could significantly affect bond formation.

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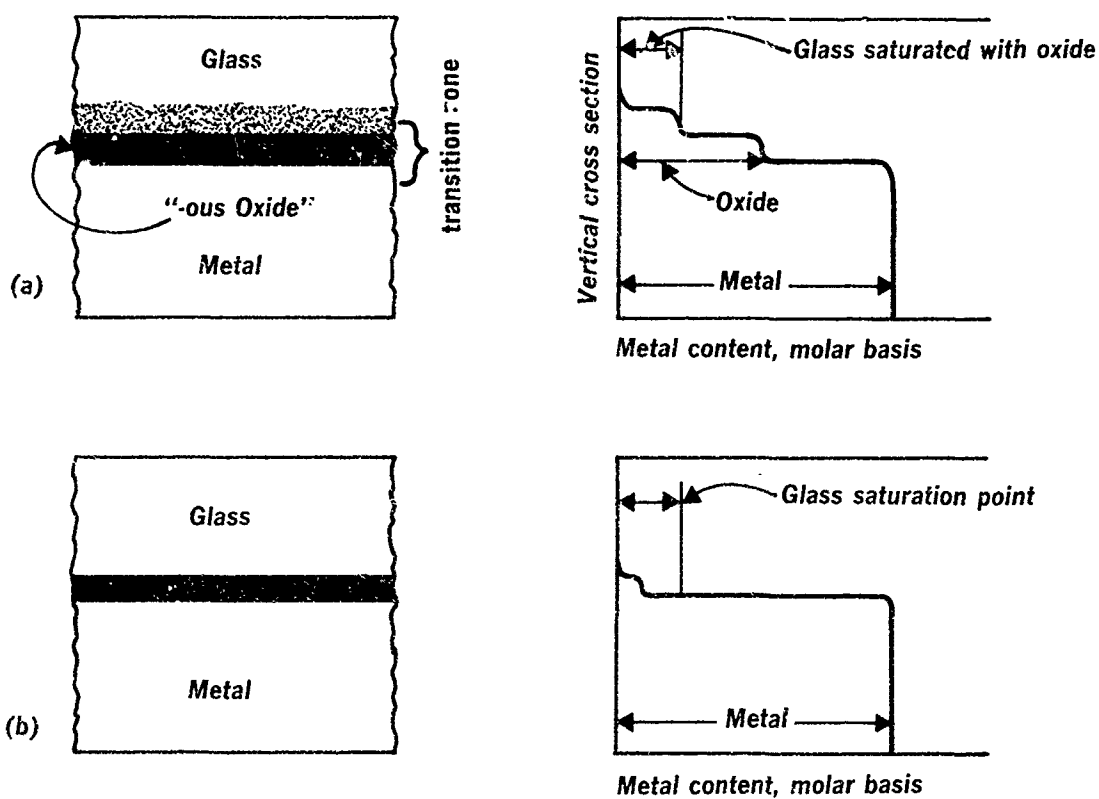
Figure 6 . — Schematic representation of glass-metal seal (a) with chemical bonding or thermodynamic equilibrium across transition zone at interface, and (b) with van der Waals type of bonding or no thermodynamic equilibrium at interface. In (a) there is a balance of bond energies in the transition zone; the "-ous oxide" layer may under these conditions be as thin as one molecule. In (b) there is no balance of bond energies at the interface. (155)

(a)

—M —M —M —O —M —O —M —O —Si —O —M —O —Si —O—

—— Metal ——————▶◀—————— "-ous Oxide" ————▶◀————— Glass ——————

—M —M —M —O —Si —O —M —O —Si —Na—

——— Metal ————————▶◀▶◀————————— Glass —————————

'-ous Oxide layer"

(b)

—M —M —M O —Si —O —Na —O —Si —O —M—

——— Metal ———————————▶◀——————————— Glass —————————
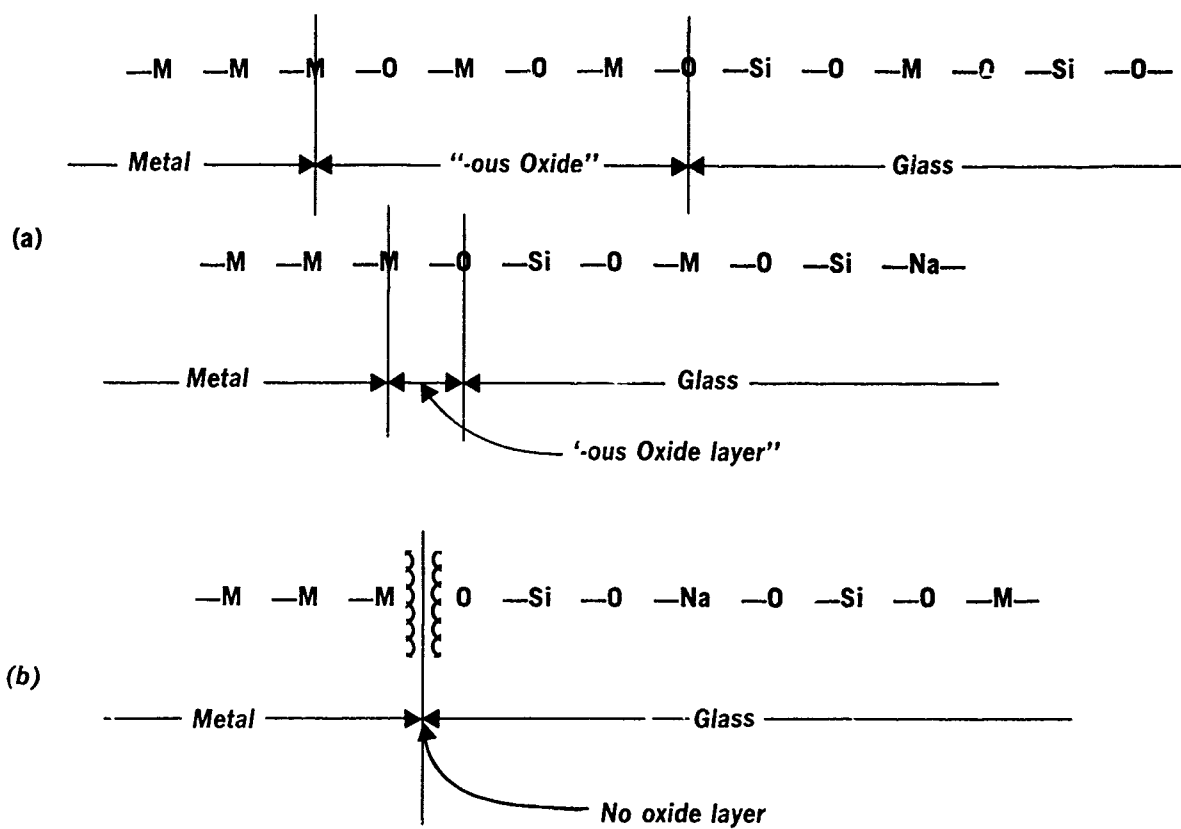
No oxide layer

Figure 7 . — Schematic representation of transition zones through metal-glass
interfaces, showing conditions for chemical and van der Waals type of bonding.
(a)   Chemical bonding with and without discrete intermediate oxide layer.
(b)   van der Waals type of bonding. (155)

Among the basic variables which must be considered are:

(1) Temperature
(2) Time
(3) Ceramic and metal compositions
  (a) Primary phases or major constituents
  (b) Grain boundary impurities
  (c) Lattice impurities
(4) Grain size and orientation
(5) Surface roughness
  (a) From deformation of the surface
  (b) From chemical attack of the surface
(6) Lattice structure
  (a) Spacing of atoms and associated fields in crystalline planes
  (b) Imperfections (including impurities) distorting the lattice and/or leaving vacant sites
(7) Surface contamination
  (a) Particles sitting on the surface
  (b) Adsorbed films and particles
(8) Stresses
  (a) Resulting from thermal expansion differences
  (b) Epitaxially induced

Since the relation of only a few of these to bond formation have been examined, it is not at all surprising that the investigators have thus far been unable to present an acceptable atomistic theory of ceramic-metal bonding.

6.4 Suggested Future Investigations

Since the roles of the large number of variables which affect the preparation of ceramic-metal joints are not fully clear, it is suggested that a program be conducted to study the influence of the variables and their interactions on the formation of ceramic-metal joints. Once this is understood the problems of controlling joint reliability, improving joining techniques, formulating new metallizing compositions and constructing an acceptable bond theory will be greatly simplified. In the initial phase of such an investigation as many of the variables as possible should be eliminated and those which cannot be eliminated should be controlled as closely as possible. Proper statistical design of the experiments should help in identification of the effects produced by the variables and their interactions.

Experiments should be conducted involving clean atomically smooth surfaces such as the freshly-cleaved surfaces of high-purity single crystal ceramics in high vacuum. The effects of crystal orientation should be studied. The formation of a bond by liquid, vapor, and solid-state processes should be compared using appropriate investigative techniques such as electron microscopy, X-ray or electron diffraction and radioactive tracer analysis. To study the effects of stress, varying thicknesses of vapor deposited films may be applied to clear single crystal substrates at several temperatures and the strains produced may be measured optically. Such experiments should also be conducted on pure oxide glasses since the manner of stress release is different when glide planes are absent as in the random glass network. Subsequent

or parallel experiments should be made on polycrystalline ceramics with varying grain sizes and impurity concentrations. All experiments must be conducted under controlled atmospheric conditions and the influence of atmosphere must be examined quantitatively.

In the course of the investigation each variable should be studied both separately and in relation to its possible interaction with other variables to obtain thorough understanding of their effects on the strength of ceramic-to-metal joints. The final goal of such a program would be not only to establish the factors necessary to obtain good bonding in essentially any ceramic-metal system, but to formulate a complete theory of the bond formation on the basis of this knowledge.

7. Summary and Conclusions

Commercial methods of effecting ceramic-to-metal joints are based on processes which were disclosed more than a decade ago. However, there have been no important applications which could not be accomplished by the available joining methods. In the past decade, no completely novel joining technique has been developed but the new product requirements and reliability have fostered process simplification and improvement. This general improvement coupled with the search for an ideal process will continue to nurture process development.

In the design and use of ceramic-to-metal joints, the main problems stem from the fact that ceramics are brittle and a scientific approach to design has not been encouraged. Commercial ceramic components are formulated with more consideration for ease of fabrication than for the properties of the material. Applications of outstanding high temperature properties of many ceramic compounds have not been realized because of the scarcity of reliable property data. The collection of the available data into a ceramic handbook is urgently needed for improved designs. Property data for metals is more complete and more readily available than for ceramics but, in the future, an extension of the capabilities of metals will be important. A ceramic-to-metal joint must be considered as a package from a design and materials standpoint. A deficiency in any one component, whether a major part or an accessory material, will be reflected as a weakness in the whole assembly.

Very little unique equipment exists in the ceramic-to-metal joining field and any distinctive apparatus in use has been developed for metallizing. While the economic advantage of the prevalent sharing of equipment with other disciplines cannot be questioned, the dangers of cross-contamination, inadequacy of facilities, and abuse of equipment capabilities is always present. Unless a novel fabrication method is developed there is little likelihood that unique equipment for ceramic-to-metal joining will be developed.

In the ceramic-to-metal joining field as a whole, the greatest need is for a dual standard of testing which will generate basic and comparative property data. The investigation of true property values requires a precise, accurate, reproducible set of testing methods. The comparison tests must be simple, inexpensive, and require little expenditure of time with semi-skilled labor while producing not necessarily absolute but reproducible data. The greatest needs are in mechanical testing methods which, in the past, were usually adaptions of methods established for metals but not for assemblies containing brittle ceramics. In all cases, including specialized tests, emphasis is required on failure analysis and standard testing procedures.

The concepts which some authors have listed as ceramic-to-metal bonding theories are little more than explanations of observed phenomena. A less empirical approach to ceramic-metal joining theory which is based on fundamental adhesion concepts and takes into account related fields is required.

The most important observation in a consideration of ceramic-to-metal joining theory is the relatively low observed strength of all joints compared

to the strength of even a van der Waal type bond. It is recommended that systematic basic research be undertaken to assess the effects of incomplete interactions, internal stresses and faulty testing. This basic research should necessarily take the form of an interdisciplinary study of the large number of variables which are important in joining with statistically designed experiments to provide an adequate knowledge of the true bonding mechanisms.

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13 ABSTRACT

A state-of-the-art review of the joining of crystalline ceramic parts to metal parts is presented. This study was undertaken to evaluate the current status of ceramic-metal joining, particularly in relation to its advancement in the past decade, and to develop unifying principles which could lead to more effective joining techniques. The mechanical and chemical methods used in the fabrication of structural and electronic components, with and without hermetic requirements, were considered including the general requirements and limitations of the components without regard to specific areas of utility.

All major facets of the technology were covered under joining techniques, materials, apparatus, theories and test methods. Background information was obtained from an extensive survey of domestic and foreign literature and from field research based on a questionnaire survey and personal interviews. On the basis of the information collected, each major aspect of the technology is critically reviewed and recommendations for future improvements are advanced in this report.

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